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THE TEMPERATURE COEFFICIENT OF RESISTANCE OF METALS AT CONSTANT VOLUME AND ITS BEARING ON THE THEORY OF METALLIC CONDUCTION.[1]

By Charles A. Kraus.

IT is a well established fact that, excepting at very low temperatures, the resistance of pure metals increases very nearly as a linear function of the temperature.[2] If we grant the postulate that the electric current consists in a transfer of electricity in the form of discrete charges, it obviously follows that a change in resistance must be due either to a change in the number of carriers or to a change in their speed. In the theoretical treatment of the problem of metallic conduction it is usually assumed or implied that the number of carriers in a metal is independent of the temperature. This assumption greatly simplifies the treatment of the problem, but, as will be shown below, such an assumption is not always justified.

If the current in metals is carried by the negative electrons, then some manner of equilibrium must exist between the negative electrons, the positively charged residuals, and the neutral molecules. To what extent the metal atoms are dissociated is still an open question. Unless the dissociation is very high, the influence of temperature on the dissociation process must make itself felt; but whether the dissociation increases or decreases with increasing temperature is a question that can not be answered *a priori* either in the affirmative or negative. On the one hand, as in the case of many homogeneous equilibria with which we are familiar, the dissociation may increase with increasing temperature,

[1] Contributions from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 99.

[2] There are numerous cases where the resistance-temperature curve passes through a minimum instead of approaching a zero value as the temperature approaches the absolute zero. This abnormal course of the curve is doubtless due to the presence of impurities. The nature of the phenomenon underlying the action of impurities on the resistance is as yet unknown.

while, on the other hand, metallic systems may behave analogous to electrolytic solutions, in which case the dissociation as a rule decreases with increasing temperature. It is to be borne in mind that the metals constitute highly condensed systems and that therefore a very small change in physical condition may have a large influence on the equilibrium in question. Thus, for example, temperature change is accompanied by change in density and it will be shown below that the change in the resistance of metals with temperature is in a large measure a consequence of the accompanying density change.

If the conduction of the current is due to electrons having a considerable freedom of motion in the body of the metal, then, other factors remaining equal, the resistance should increase with increasing temperature, since the frequency of collision increases with temperature according to the kinetic theory. The general form of the resistance-temperature curve of metals is therefore in harmony with the usual theory of metallic conduction. The fact should not be overlooked, however, that the observed resistance change is a resultant effect of all factors concerned among which are included effects due to volume change.

It is evident that with decreasing volume, the number of collisions per unit of time will increase and that the resistance will therefore increase. On the other hand, in most cases, it is found that the resistance actually decreases. The number of carriers under these conditions must therefore increase by an amount more than enough to compensate the decrease in resistance due to the increase in the number of collisions.

In determining the influence of volume change on the number of carriers present in a metal the obvious course is to determine the resistance of the metal at different temperatures keeping the volume constant. Without going into a detailed discussion, it is evident that with increasing density of a metal the number of carriers may be expected to increase. For example, in the case of mercury we know that the vapor is a non-conductor. If we were able to pass mercury through the critical state, we would doubtless find a continuous gradation of conducting power all the way from that of metallic liquid mercury to non-conducting mercury vapor. Similarly, when a metal is dissolved in a non-metallic solvent, we have a continuous gradation of conductance from that of a highly conducting metal to that of a poorly conducting solution.[1] So also, metals which melt with decrease of density increase in resistance on melting, while metals which melt with increase of density decrease in resistance on melting.

[1] In this case, however, the condition approached as the metal becomes highly attenuated is materially modified by the presence of the solvent medium in which the metal is imbedded. Kraus, Trans. Am. Electroch. Soc. *21*, 119 (1912).

Data are available for calculating the resistance-temperature coefficient at constant volume for a number of metals. With the exception of mercury, all are solids. Taking into account the crystalline structure of solid metals, the influence of pressure on their resistance can not be interpreted with certainty. In the case of mercury, however, we have a metallic system of very simple molecular structure the results with which may be interpreted unambiguously if our kinetic conceptions regarding metals have any foundation in fact.

The temperature coefficient of resistance of a metal at constant volume is given by the equation:

$$\frac{\partial R/R}{\partial T} = \frac{dR/R}{dT} - \frac{\partial R/R}{\partial p} \cdot \frac{\partial v/v}{\partial T} \Big/ \frac{\partial v/v}{\partial p}.$$

The values of the last four coefficients have previously been measured and found to be as follows for liquid mercury at 20° and at one atmosphere pressure:

$$\frac{dR/R}{dT} = 8.9 \times 10^{-4}; \quad \frac{\partial R/R}{\partial p} = -3.3 \times 10^{-5}; \quad \frac{\partial v/v}{\partial T} = 1.82 \times 10^{-4};$$

$$\frac{\partial v/v}{\partial p} = -3.8 \times 10^{-6}.$$

From these we find by calculation

$$\frac{\partial R/R}{\partial T} = -6.9 \times 10^{-4}.$$

This result shows that when liquid mercury at 20° is heated at constant volume its resistance *decreases* by 0.069 per cent. per degree, whereas when heated at constant pressure its resistance increases 0.089 per cent. per degree.

The result obtained above for the resistance-temperature coefficient of liquid mercury at constant volume is very significant and admits of only one interpretation, namely: *the increase in resistance of liquid mercury with increasing temperature is due to its decrease in density.* The total resistance change due to density change is 0.156 per cent. per degree.

Since the influence of increasing temperature, according to kinetic conceptions, is to increase the resistance of a metal, owing to reduction of the mean free path, and since at constant volume the resistance of liquid mercury decreases with increasing temperature, it follows that *at constant volume the number of carriers in liquid mercury increases with the temperature.*

If carriers are present in metals at all, they must be in some manner of equilibrium with each other and with the neutral molecules from which

they are derived. This equilibrium is controlled by two main factors, namely: density and temperature, and these two factors influence the equilibrium in opposite directions. The dependence of the equilibrium on temperature and density is in entire conformity with our knowledge of equilibria in general and in particular with electrolytic equilibria. For example, the enormous decrease in the dissociation of electrolyte with increasing temperatures is in very considerable measure due to the decrease in the density of the solvent with increasing temperature. This is well illustrated by solutions of potassium iodide in methyl alcohol beyond the critical point where, for constant concentration of the electrolytes, the conductance increases enormously with increasing density of the solvent.[1]

The magnitude of the effect of density on the conductance of mercury has a very important bearing on the question as to the number of carriers present in liquid mercury. In many cases there has been a tendency to assume that the number of electrons present in a metal is of the order of the number of atoms present. From the foregoing data, we see that on heating liquid mercury at constant volume the number of carriers increases at least 0.07 per cent. per degree.[2] Such an increase in the number of carriers could not result if the metallic atoms were even approximately completely ionized. We must therefore conclude that *only a small fraction of the atoms of liquid mercury are ionized and furnish carriers for the current.*

The foregoing considerations would appear to demonstrate the necessity for considering the equilibrium between the changed carriers in a metal and the neutral atoms in any theory of metallic conduction which is founded on kinetic considerations. To do this, however, presents great difficulties. It need only be recalled that the corresponding problem is as yet only very incompletely solved in the case of ordinary electrolytes, where the conditions apparently are much simpler than in metals. The whole question of equilibria in systems of charged particles requires fundamental study and there is little hope that the problem of metallic conduction will be solved from a theoretical standpoint until such studies are forthcoming. The lack of tangible results in the problem of metallic conduction and of the metallic state in general is ample proof of the inadequacy of present day conceptions respecting this subject.

BOSTON, March, 1914.

[1] Kraus, this Journal, *18*, 101 (1904.)

[2] If we assume that the decrease in translatory speed is proportional to the square root of the absolute temperature, the resistance decrease per degree due to this cause is 0.18 per cent. per degree. The increase in the number of carriers on this basis would therefore be 0.25 per cent. per degree.

SOME EFFECTS OF DIFFRACTION ON BRIGHTNESS MEASUREMENTS MADE WITH THE HOLBORN-KURLBAUM OPTICAL PYROMETER.

By A. G. Worthing and W. E. Forsythe.

Introduction.

THE study of the properties of many substances at high temperatures is often conveniently carried out with the substance mounted as a filament in a lamp bulb. Ordinarily such filaments will be small. In such cases particularly, in the opinion of the writers, the only method of optical pyrometry both convenient and theoretically safe which may be employed as an aid, is that one on which the Holborn-Kurlbaum pyrometer is based. Its underlying principles as described by the originators[1] are simple. Essentially as is indicated in Fig. 1, an image of a background *A* is formed by the lens *B* in the plane of a filament *D* which may be heated to incandescence. This filament will be referred to as the pyrometer filament. An eyepiece *F* backed with an approximately monochromatic glass filter *G* is used to view the pyrometer filament thus seen projected against the background. By varying the current through the pyrometer filament, it may under suitable conditions be made to match the background image in brightness, that is to disappear against the background. Evidently various backgrounds may be compared.

In attempting to determine the temperature of a certain tungsten lamp filament, first using an ordinary commercial Holborn-Kurlbaum pyrometer and then a modified one such as will be described in this paper both of which had been calibrated against the same black body, a difference of about 40° in temperature was obtained with the filament at about 2,300° Kelvin. This difference was too much to be ascribed to errors in measurement. An investigation of the causes has led to interesting results.

Arrangement of Apparatus.

The apparatus as arranged is indicated in Fig. 1. Large filament tungsten and carbon lamps served at various times for the background *A*. *B*, the objective lens, was a Zeiss-Tessar lens with a 28 mm. aperture and

[1] E. Holborn and F. Kurlbaum, Ann. d. Phys., Vol. 10, p. 22, 1903; Ber. d. K. Akad. d. Wiss., Vol. 30, p. 712, 1901.

a 21 cm. focal length. The entrance cone aperture in the diaphragm C was variable in size and circular in shape. Its actual location was between the component parts of the lens B. As pyrometer filaments at D various carbon, tungsten, and platinum filaments of different sizes were used. An ordinary piece of sheet metal with a circular aperature served as the diaphragm E. Various telescopes were used for the eyepiece F. As monochromatic glass filters, pieces of ruby and of blue uviol glass having maximums of transmissions respectively at about $\lambda = 0.66\mu$

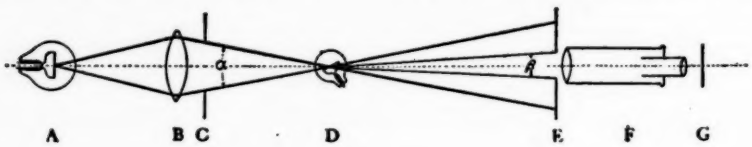

Fig. 1.

Diagram showing arrangement of apparatus. A, background; B, objective lens; C, entrance cone diaphragm; D, pyrometer filament; E, eyepiece diaphragm; F, eyepiece; G, monochromatic filter.

and at $\lambda = 0.46\mu$, were used. The various parts of the apparatus were independently adjustable and during the course of the work many shifts were made. Throughout great care was taken to see that the radiation from the background entirely filled the aperture at E, in other words to see that the angle α always exceeded the angle β, and to see that the apparatus was alined axially.

EXPERIMENTAL RESULTS.

A large part of the work consisted in determining the apparent variations in the ratio of the brightness of the pyrometer filament to the brightness of the background image formed in its plane as functions of α. In this connection there were determined the various currents through the pyrometer filament at apparent brightness matches, corresponding to the various values of α. By means of similar measurements made with various sectored discs between C and D and with the aperture at C constant, it was possible to calibrate the brightness of the pyrometer filament in terms of the current passing through it, and thus to reduce the previously determined filament currents to filament brightnesses.

The results thus obtained for a particular arrangement of apparatus (AB = 25 cms.; BD = 128 cms.; DE = 185 cms.; diameter of aperture at E = 9 mm.) for a succession of values of α, when various pyrometer filaments were successively substituted at D, are presented in Fig. 2. The method of obtaining the actual value of the ratio platted as ordinates

will be discussed later. It is sufficient to consider at present the relative variations occurring in the curves for each individual pyrometer filament. In each instance decreasing the entrance cone angle α apparently de-

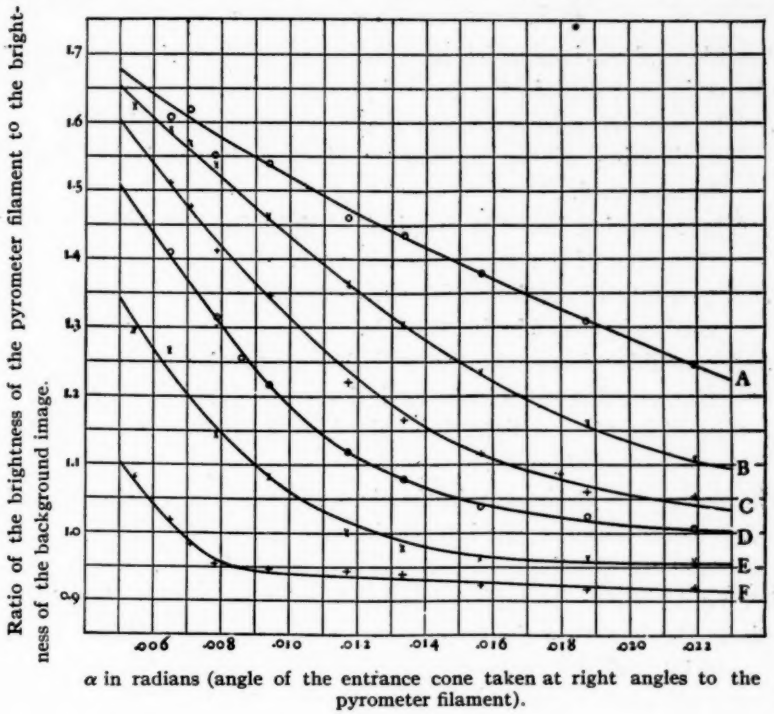

Fig. 2.

Variations in the apparent brightness of the background image with α for various sized pyrometer filaments.

Curve.	Diameter of Pyrometer Filament.	Material of Pyrometer Filament.	Average Wave-length of Light Used.
A	0.016 mm.	tungsten	0.66
B	0.025 mm.	"	0.66
C	0.025 mm.	"	0.46
D	0.045 mm.	carbon	0.66
E	0.050 mm.	tungsten	0.66
F	0.100 mm.	"	0.66

creased the brightness of the pyrometer filament or increased the brightness of the background. Evidently no actual changes in the brightness of the pyrometer filament or of the background could be thus produced. There is also a change in this variation depending upon the size of the pyrometer filament but no change to any appreciable extent depending upon the material of the filament. Further, curves *B* and *C* indicate

that the variations are different for the same pyrometer filament when different colored lights are used.

SUGGESTED EXPLANATIONS.

Possible explanations which have occurred to the writers which might wholly or in part explain the general phenomena are:

1st. The lens and mirror actions of the pyrometer lamp bulb.

2d. The heating of the pyrometer filament by radiation from the background.

3d. The reflection into the eyepiece of light from the background at the edges of the pyrometer filament.

4th. A possible transmission by the pyrometer filament of light from the background incident on it.

5th. A possible change in the emissive properties of the pyrometer filament due to incident radiation from the background.

6th. The diffraction of light from the background at the edges of the pyrometer filament.

The using of a platinum wire in air free from an enclosing glass bulb as a pyrometer filament, the interposing of a water cell between A and D, the geometrical consideration of the areas of the pyrometer filament which could serve as surfaces reflecting incident radiation into the eyepiece, the fact that the effect noted was found to be independent of the material and the temperature of the pyrometer filament, and the fact that the effect noted was found with the aid of variable rectangular apertures at C to depend upon the angle of the entrance cone of radiation taken in a plane normal to the pyrometer filament and not at all upon the angle taken in a plane parallel to it, respectively showed that the first five suggested explanations could not account for the variation noted. None of these modifications have yielded results inconsistent with diffraction as an explanation, in fact the results obtained with the rectangular apertures at C form positive evidence in its favor.

Experiments by Gouy[1] on the diffraction of unpolarized light by a sharp edge, indicated that the light which was bent by diffraction into the geometrical shadow, was partially polarized in the plane parallel to the edge. With this in mind there were made some tests exactly similar to those already described in which polarized light was used. A nicol introduced just in front of the apertures at E was first set so that the plane of polarization was parallel to the pyrometer filament and then later at right-angles to it. A large carbon filament whose position was so oriented that the pyrometer filament was always seen projected along

[1] C. R., Vol. 98, p. 1573, 1884.

the center of and parallel to its image, was used as the background. This insured that the brightness of the background would be the same in the two cases. For a given relatively large aperture at C, the larger current was required through the pyrometer filament for an apparent brightness match in the case where the plane of polarization was perpendicular to the pyrometer filament. In this same case when the aperture at C was decreased to some relatively small value, the apparent relative change in brightness was less than with light polarized parallel to the filament. This is consistent with the results of Gouy noted above, on the assumption that the diffracted light to which the apparent changes in brightness are ascribed, was for the most part made up of light which had been bent by diffraction into the geometrical shadow. This assumption as will be noted later, was experimentally verified. The differences found in the apparent relative brightnesses of the pyrometer filament of tungsten for the two conditions of polarization noted, indicated an apparent polarization of 20 per cent. in the light from it. Taking into consideration the polarization of the light from the background which is diffracted, this is consistent with the value of 12 per cent. which may be obtained from data which have already been published by one of the writers.[1]

If from the central part of the aperture at C, one blocks out a region such that from a consideration of geometrical optics only, none of the light coming from the background in the immediate neighborhood of the place where the pyrometer filament is seen projected can enter the aperture at E, and if no current is passed through the pyrometer filament, one can still see the filament apparently glowing where it crosses the background image when looking at it through the eyepiece. In case the resolving power of the eyepiece is sufficiently great, this apparent brightness of the pyrometer filament is seen to consist of two bright streaks along the edges. Whether or not the axes of these bright streaks actually lie within or without the boundaries of the pyrometer filament is very difficult of determination. The fact that with eyepieces of small resolving power they seem to cover the entire filament and more is due largely to irradiation. A photograph of such a case is shown in Fig. 3, *a*. Fig. 3, *b* indicates a similar condition in which case, however, the pyrometer filament was rendered visible by means of a small current. By blocking out first the upper and then the lower portions of the remaining part of the aperture at C, it was easily demonstrable that this light consisted largely of light which was bent by diffraction into the geometrical shadow, and but to a comparatively small extent to light which was diffracted in the other direction.

[1] A. G. Worthing, Astrophys. Jour., Vol. 34, p. 345, 1912.

The apparent brightness which these lines of diffracted light gave to the pyrometer filament were found to account in magnitude for the variations noted. By means of an extra lens and an extra pyrometer filament located between D and E (Fig. 1), there were measured first the apparent brightness of the unheated pyrometer filament at D due to

Fig. 3.

Photographs showing apparent brightness of pyrometer filament due to light from the background diffracted by it. *a*, pyrometer filament cold; *b*, pyrometer filament made luminous by a small current.

this diffracted light when the central part of the aperture at C was blocked out as just noted, and then the apparent brightness of the heated pyrometer filament when the aperture at C was equal to that portion which previously had been blocked out. The results for three such cases are given in Table 1. The agreement in the brightness sums was better than one could reasonably expect.

TABLE I.

Effects of the Different Elements of the Entrance Cone of Radiation on the Apparent Brightness of a 0.050 mm. Tungsten Pyrometer Filament.

Outer Edge of Lens Screened Off.		Central Part of Lens Screened Off.		Brightness Sums.
Angles Subtended by Central Opening.	Relative Brightness of Pyrometer Filament.	Angle Subtended by Central Screen.	Relative Brightness of Pyrometer Filament.	
0.012 radians	0.755	0.012 radians	0.240	0.995
0.028	0.888	0.028	0.117	1.005
0.038	0.936	0.038	0.064	1.000

The results with rectangular apertures at C led to the trying of similar apertures at E. In this case with the aperture at C circular, some small variations were found only when the aperture was varied in a direction parallel to the pyrometer filament. These were accounted for in magnitude and direction by computations based on the fact that as the aper-

ture at E was thus enlarged the average value of the entrance cone angle α was diminished.

The results obtained with the rectangular apertures at C, the obtaining of results with the aid of polarized light which are consistent with previously obtained results, the resolution of the apparent added brightness of the pyrometer filament in certain cases into two narrow lines of light along its edge, and the accounting in magnitude for the variations in brightness of the pyrometer filament by means of the apparent added brightness due to these narrow lines of light seem to indicate conclusively that the phenomena are wholly due to diffraction.

RELATION BETWEEN THE BRIGHTNESS OF THE PYROMETER FILAMENT AND THAT OF THE BACKGROUND IMAGE.

The condition usually assumed as holding in optical pyrometry is that the ratio of the brightness of the pyrometer filament to that of the background image formed in its plane *is* unity when there is an apparent brightness match. The present work shows this in general to be untrue. Actual determinations of this ratio which for brevity's sake we shall denote by k have been made. The method of doing this is theoretically simple. Three lamps whose filaments are represented here by 1, 2 and 3 were used, filament 1 being the pyrometer filament for which for a given entrance cone angle α, it was desirable to find k. With filaments 1 and 2 as pyrometer filament and background respectively, an apparent brightness match was obtained and their currents measured. Then, using these filaments successively as backgrounds, carrying the currents just determined, their brightnesses were compared with the aid of a pyrometer filament (filament 3) whose brightness-current relation had previously been determined as described above. Due consideration was of course necessarily given to the transmissions of the lens and of the individual lamp bulbs. Considerable difficulty is experienced experimentally in case filament l is small. This is due to the fact that it is very difficult to make pyrometer settings when the image of the background is small, as was the case with lamp l in most of our attempts to determine this ratio k. For the lamps used in obtaining the data presented in Fig. 2, we have determined with considerable care the corresponding values of k for an angle α equal to 0.0182 radians. These values of k have been used in locating the curves definitely in Fig. 2. Attention is once more called to the fact that the curves as platted actually represent the ratio of the brightness of the pyrometer filament to the brightness of the background image formed in its plane. In some instances as indicated the pyrometer filament is not as bright as the background image but in

general the pyrometer filament is seen to be considerably brighter. For the lamps *A* and *B* that were used the transmission of single thicknesses of the lamp bulbs was approximately 91 per cent. The transmission of the lens used was 77 per cent. It is readily seen that when the lamps *A* and *B* were used as pyrometer filaments for small values of the entrance cone angle α, in the neighborhood of 0.006 radians, the pyrometer filament was brighter than the filament used in the background itself, although the background was viewed through several more thicknesses of glass than was the pyrometer filament.

Some determinations of k made under conditions when angle α was of the order of 0.1 of a radian, indicated that, if the curves in Fig. 2 could be prolonged, they would finally become asymptotic to a value for the relative brightness in the neighborhood of 91 per cent. or 92 per cent. These measurements were attended with considerable difficulty, however, and should not be relied upon too fully. This k which represents the ratio of the brightness of the pyrometer filament to the brightness of the background image when they appear of equal brightness, as may be seen from the curves of Fig. 2, is dependent on the angle α, the diameter of the pyrometer filament and the character of the light used but apparently not to any appreciable extent upon the character of the material of the pyrometer filament.

It was of interest to find out in this connection whether the size of the background had an effect or not. It was thought sufficient to equate by the color match method as described by Hyde[1] the brightnesses of two very different-sized filaments of the same material which were to be used as backgrounds and then to compare their brightnesses with a given pyrometer filament. As two such backgrounds a 0.25 mm. and a 0.016 mm. tungsten filament were used. The two methods gave identical results. A trial with two other filaments not differing as widely in diameter gave like results. From this it may be concluded that k is independent of the size of the background, as one might naturally expect.

Appearance of a Pyrometer Filament as Seen Projected Against the Background.

There are to be distinguished here three cases; 1st. When the entrance cone angle α is relatively large. 2d. When it is relatively small. 3d. When it is very small. In Fig. 4 we have given for such cases schematic diagrams illustrating certain apparent brightness variations in the neighborhood of the intersection of a 0.025 mm. tungsten pyrometer

[1] Astrophys. Jour., 36, p. 89, 1912.

filament with the background image when the condition is fulfilled that the pyrometer filament shall disappear against the background image, in case the resolving power of the eyepiece is sufficiently small to permit of it. For simplicity the variation from Lambert's cosine law of the radiation from the pyrometer filament is here disregarded. The diagrams themselves, however, indicate what may be seen when, with the pyrometer lamp adjusted for such disappearance, we use an eyepiece arrangement with a considerably higher resolving power so that greater

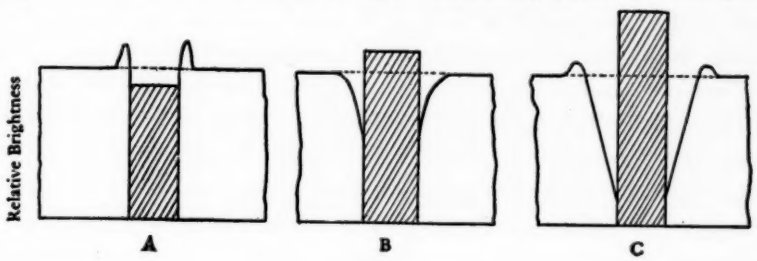

Fig. 4.

Distances along the background image. Schematic diagrams for illustrating certain apparent brightness variations in the neighborhood of the intersection of a 0.025 mm. tungsten pyrometer filament with the background image. Shaded portions represent the pyrometer filament; unshaded portions represent the image of the background. Case A, the entrance cone (angle α) relatively large—pyrometer filament less bright than background image; Case B, the entrance cone (angle α) relatively small—pyrometer filament brighter than background image; Case C, the entrance cone (angle α) relatively very small—pyrometer filament much brighter than background image.

detail may be seen. While the diagrams indicate the bright and dark bands which may be noticed as located just outside the confines of the pyrometer filament, the exactness of this method of representation should not be too strongly insisted upon. When the entrance cone is relatively large (case *A*) the pyrometer filament is less bright than the background image and, in case the resolving power of the eyepiece is sufficient, bright lines may be seen along the edges of the pyrometer filament. Of course these bright lines are quite disconcerting when one is attempting to make pyrometer settings.

In case a somewhat smaller cone angle α is used, these bright lines disappear so that even with an eyepiece of fairly high resolving power one does not have any trouble in obtaining a perfect disappearance of the pyrometer filament against the background image. The exact explanation of the dark bands noted in cases *B* and *C* and of the extra bright bands in case *C* are not at once apparent though we think they should also be ascribed to diffraction at the pyrometer filament. What has been said thus far as to the appearance of the pyrometer filament, refers strictly to a

tungsten pyrometer filament about 0.025 mm. in diameter. The general appearance when using larger pyrometer filaments are exactly similar so far as the eye can discern. However, in view of the results obtained on the ratio of the brightness of the pyrometer filament to the brightness of the background image (Fig. 2), the general description as to relative brightnesses for the three cases must here be modified, for the dark bands along the edges may be seen when the pyrometer filament is not as bright as the background image. The explanation which occurs to the writers is that the condition in such a case is somewhat similar to what has been represented above for case *C*, though the two outer bright bands are not observable. Such a condition may readily be correlated with the relative brightnesses observed. Of course, it is probable that with the 0.025 mm. pyrometer filament in case *B*, the extra bright bands of case *C* are also present though not observable.

This type of diffraction, in which the diffraction fringes are located in the plane of the diffracting edge, so far as the writers know has not been studied heretofore, seems to be an important type and to be well worth further study.

The fact that disappearance can be obtained under such conditions as have been described when an eyepiece with low resolving power is used, is due to the fact that the eye averages the brightness variations over a considerable angular range. Many times in our work we have been able to go from impossible working conditions to fairly satisfactory conditions by substituting for the eyepiece in use, one of lower resolving power.

SOME NECESSARY WORKING PRECAUTIONS.

In view of the results which have been obtained and the difficulties which have been experienced, certain conclusions are definitely reached regarding necessary working precautions. In case one wishes to compare various light sources, excepting possibly where the entrance cone angle α is comparatively large, that is of the order at least of 0.1 of a radian:

1. The sources to be studied should be used as backgrounds and not as pyrometer filaments.

2. A single pyrometer filament should be used throughout the intercomparison.

3. The angles α and β should be definitely fixed. This can be best done by having limiting diaphragms at *C* and *E* which are at fixed distances from the pyrometer filament preferably as far away as possible. A commercial pyrometer of the Holborn-Kurlbaum type which we have in our laboratory possesses fixed diaphragms but they are in no sense limiting diaphragms.

4. The apparatus should be so adjusted that there is approximately axial symmetry.

5. The resolving power of the eyepiece should not be so great as to prevent the practical disappearance of the pyrometer filament against the background image.

6. The image of the background should be large in comparison with the pyrometer filament.

7. The magnifying power of the eyepiece should be sufficiently large so that no difficulty is experienced by the observer in fixing on the intersection and so that effects due to the eye's imperfections are largely eliminated.

It is interesting to note in this connection that the 40° difference in temperature, which as has been noted in the introduction was the starting point of the present paper, was apparently largely due to a failure to appreciate the importance of working precautions Nos. (6) and (7).

Some Desirable Working Conditions.

1. It is obvious that the eyepiece should have as high a resolving power as possible but still with the condition that when the pyrometer lamp is balanced against the background there shall be disappearance. The ideal case is obtained when no matter how great the resolving power of the eyepiece neither bright nor dark bands may be seen at the edge of the pyrometer filament. This condition of disappearance depends upon the size of the pyrometer filament, upon the value of the angle α, and in case the deviations from Lambert's cosine law are not neglected upon the material of the pyrometer filament. Using pyrometer filaments of tungsten, the writers have roughly attempted to find these conditions. For a 0.050 mm. tungsten pyrometer filament using red light, a very satisfactory value for the entrance cone angle α was found to be 0.05 radian. Smaller pyrometer filaments require somewhat larger entrance cone angles, while larger pyrometer filaments require smaller entrance cone angles. This is not entirely in conformity with what would be deduced from Fig. 2, assuming that the most satisfactory value for α is that which corresponds to the condition that the pyrometer filament is very nearly of the same brightness as the background image when there is an apparent brightness match. This has been discussed above under the heading relating to the appearance of the pyrometer filament. It should not be forgotten, however, that for a considerable range on either side of such values, the disappearances will be very satisfactory, and that even when the disappearances are not satisfactory with a certain eyepiece very satisfactory disappearances may be obtained with eyepieces

of smaller resolving power. Sometimes, particularly when it is necessary to use a highly magnified background image, a small pyrometer filament is better than a large one, because for a given large magnification due to the eyepiece the bright or the dark bands will be less apparent for the smaller filament. This is due to the fact that for a given eyepiece resolving power the range of good disappearances for the smaller filament considerably overlaps that of the larger.

2. An eyepiece and eyepiece diaphragm combination which gives comparatively large clear images is of course desirable. A short focus objective lens for the eyepiece and as large an aperture as possible in the diaphragm are necessary to reduce to a minimum the diffraction of the light which occurs at the eyepiece diaphragm. Using light of short wave-length is advantageous here.

3. The pyrometer lamp is important. In general the writers have found filaments in either hairpin loops or single straight filaments mounted in spherical bulbs to be most satisfactory. In general in any particular problem the pyrometer filament should be considerably smaller than the filament of the background. In some cases carbon may be preferable to tungsten for pyrometer filaments. In other cases the reverse is true. Due to the deviations of the emissions from Lambert's cosine law as described by one of the writers[1] one might expect in general to be able to use carbon filaments advantageously when the entrance cone angle α is large and tungsten filaments when this angle is small. So far as the writers can see there is but little advantage of the one over the other based on the supposition that the relative change in brightness for a given relative change in current is greater for one type of filament than for the other. Whatever advantage there may be of this nature is apparently in favor of the untreated carbon filament and is of the order of 5 per cent. In case small angles of α are necessitated, there is no question but that it is much more desirable to have pyrometer filaments of tungsten than of carbon.

4. For the sake of ease of adjustment particularly in obtaining axial symmetry, it is very desirable to have the diaphragm C one with a variable aperture.

5. In cases where high accuracy is demanded, a gain may be made in case the brightnesses permit, by using light of the shorter wave-lengths. Not only are some diffraction effects eliminated but also an actual gain is experienced due to the fact that, while for both red and blue light the least relative change in brightness which is just detectable is about the same, the relative change in brightness for a given small change in temperature is the greater for the shorter wave-length light.

[1] A. G. Worthing, Astrophys. Jour., 36, 345, 1912.

EFFECTS OF PRESENT RESULTS ON PREVIOUS WORK.

It seems natural in this connection to consider what effect the present work may have on the results of other investigations where the Holborn-Kurlbaum optical pyrometer principle has been used. An inspection of the literature shows that writers in general have not specified carefully the conditions under which their pyrometers have been used. Because of this we restrict our comments to papers with which we have been personally connected and to papers which have been issued from this laboratory.

1st. In a paper on "A Study of the Energy Losses in Electric Incandescent Lamps" by Hyde, Cady and Worthing,[1] the lamps studied were used as pyrometer lamps. Since the results on a single lamp used as a pyrometer lamp were complete in themselves, the method was free from error, and the results are undoubtedly of the right magnitude.

2d. In a paper entitled "Measurements of Intrinsic Brightness by a New Method," by Ives and Luckiesh,[2] the various sources were used as pyrometer filaments. The arrangement of the apparatus and the method employed in obtaining the brightness in which the pyrometer filament and the image of the background were assumed to be the same at a brightness match, were such that certain corrections to their results are necessary. The values obtained in most instances should be reduced by about 7 or 8 per cent. Most of them are probably relatively correct.

3d. A paper on the "Radiant Efficiency of Incandescent Filaments," by W. E. Forsythe,[3] is open to the same objection. The temperatures which were obtained were probably too high by about 1 per cent. A redetermination of these temperatures is to be undertaken in the near future in this laboratory.

4th. In a paper on "On the Deviation from Lambert's Cosine Law of the Emission from Tungsten and Carbon at Glowing Temperatures," by A. G. Worthing,[4] the method used was correct in principle.

5th. A paper "The Relation Between Black Body and True Temperatures for Tungsten, Tantalum, Molybdenum, and Carbon, and the Temperature Variation of their Reflecting Power," by C. E. Mendenhall and W. E. Forsythe;[5] the results are free from serious error due to diffraction.

SUMMARY.

1. Errors due to diffraction at the filament of the pyrometer lamp of the light from the background have been discovered in connection with

[1] Trans. of Illum. Eng. Soc. (U. S.), 6, p. 238, 1911; Illum. Eng. (London), 4, p. 389, 1911.
[2] Elec. World, 57, p. 438, 1911.
[3] PHYS. REV., 34, p. 333, 1912.
[4] Astro. Jour., 36, p. 345, 1912.
[5] Astro. Jour., 37, p. 380, 1913.

the Holborn-Kurlbaum optical pyrometer. In some cases in measuring brightnesses errors as great as 60 per cent. may occur, though in temperature measurements the corresponding errors would be much less.

2. Determinations have been made of the ratio of the brightness of the pyrometer filament to the brightness of the image of the background formed in the same plane. The use of large filaments as pyrometer filaments and large angles for the entrance cone angle α tend toward making the pyrometer filament less bright than the background image when an apparent match is obtained, conversely small filaments and small angles for the entrance cone angle α tend toward making the pyrometer filament brighter than the background image for an apparent brightness match.

3. Some necessary working precautions and some desirable working conditions for high accuracy have been considered, and may be found incorporated under appropriate subheadings of this paper.

4. The effects of the present results on certain published works have been considered.

NELA RESEARCH LABORATORY,
NATIONAL LAMP WORKS OF GENERAL ELECTRIC CO.,
NELA PARK, CLEVELAND, OHIO,
March, 1914.

THE EFFECT OF PRESSURE ON THE ABSORPTION OF LIGHT BY BROMINE AND CHLORINE, AND ITS THEORETICAL SIGNIFICANCE.

BY DAVID L. WEBSTER.

PART I. EXPERIMENTAL.

Introduction.—In this part of the paper experiments are described showing first how the visible part of the wide absorption band of bromine obeys Beer's law, that the absorption at any wave-length with a given number of molecules per unit cross-section of the beam is independent of the length of the tube through which these molecules are scattered. In the narrow bands of bromine, on the other hand, the experiments show wide deviations from Beer's law, that may be explained by the changes of width of the fine lines of which these bands are composed. In the wide band of chlorine we find a slight deviation, that may be due to chemical changes.

Since this law was first announced by Beer,[1] for solutions, many experiments have been tried to test it as applied to gases. The first exception to be found was in the visible bands of oxygen, in which the absorption by a certain amount of gas was found by Janssen[2] not to be independent of the pressure, but proportional to it.

In the infra-red, an exception was found by Ångström[3] in carbon dioxide, in which the absorption of the total radiation from a Nernst lamp increased rapidly with the pressure. A threefold increase in the absorption by carbon dioxide was found by G. Bolinder,[4] on raising the total pressure from 20 mm. to 1 atm. by adding air.

These phenomena were observed spectroscopically by Rubens and Ladenburg[5] and Ångström[6] who found the absorption at any wave-length by a given mass of carbon dioxide or monoxide dependent only on its total pressure, whether this was changed by changing the length of the tube containing the gas or by admitting air.

[1] A. Beer, Pogg. Ann., *86*, 78, 1852.
[2] Rep. Brit. Assoc., 547, 1888.
[3] Drud. Ann., *6*, 163, 1901.
[4] K. Angstrom, Arkiv for Matematik, Astronomi och Fysik, Bd. 4, No. 30, 1908.
[5] Vehr. d. D. Phys. Ges., *7*, 170, 1905.
[6] L. c.

These experiments were continued by von Bahr,[1] who extended them to many gases with results similar to those found in carbon dioxide. She found also that as the pressure was raised, the absorption increased rapidly at first, and then more slowly, approaching its maximum at a lower pressure in a heavy gas than in a light one.

In the visible spectrum, the first work after that of Janssen was by Baccei,[2] who verified Beer's law for several weakly absorbing gases, such as hydrogen sulphide and acetylene. Dufour,[3] on the contrary, found that when the total pressure on nitric peroxide or bromine vapor was raised by air, hydrogen or carbon dioxide, the fine absorption lines became hazy and were displaced by amounts proportional to the pressure. Füchtbauer[4] confirmed Dufour's results for bromine, and Wood[5] found an even larger pressure widening in mercury vapor at wave-length, 2536 A. Similar effects observed by Füchtbauer in potassium vapor and by Fredenhagen[6] in sodium were believed by these observers to be in some way connected with the increase of the ionization of the vapors by the transparent gases.

These results were interpreted by Füchtbauer as showing that the effects observed by Ångström and von Bahr were due to a widening of fine lines composing the infra-red bands, and a consequent increase of the absorption observable with the low dispersion of a spectrobolometer. Von Bahr, while agreeing that some of the bands showed evidence of such a discontinuous character, found some increase of absorption in bands that were apparently continuous. This led to the hypothesis that an increase of pressure caused an increase in the number of absorbing molecules.

An especially interesting field for exact work on pressure-absorption effects is presented by bromine vapor, because it has in the visible region a wide and apparently continuous band and also a few dozen narrow bands that may be resolved into fine lines with a moderate dispersion. Thus it gives a chance to study both types of bands in the same substance and the same part of the spectrum.

The wide band begins, according to Kayser[7] at about 3,350 A, and extends to the yellow, or even through the red if enough vapor is present, while the narrow bands occur only between 5,110 and 6,250 A, and are,

[1] Eva von Bahr, Ann. Phys. *29*, 780–96.
[2] Nuovo Cimento, *9*, 177, 1899, Beibl., *23*, 636. 1899.
[3] C. R., *145*, 173 and 757, 1907.
[4] Phys. Zeit. *12*, 722, 1911.
[5] Phil. Mag. *23*, 689, 1912.
[6] Phys. Zeit., *12*, 909, 1911.
[7] Handbuch der Spectroscopie, Vol. III., paragraph 214.

on the average, about 10 A wide and 20 apart, each one being composed of many fine lines.

Description of Apparatus.—To investigate the effects of pressure on this spectrum, I used the apparatus represented in Fig. 1. It is a modification of that of Janssen, Ångström and von Bahr. A is a Schuchert arc lamp, which may be made to give a very steady light. W is a water cell, which was sometimes filled with water to absorb merely the infrared and prevent heating of the nicols, N and N', and sometimes with a copper sulphate solution to absorb the red and yellow as far as 5,800 A. W', full of cobalt chloride dissolved in acetone (recommended by Uhler and Wood), was sometimes used to remove the red end as far as 5,450 A.

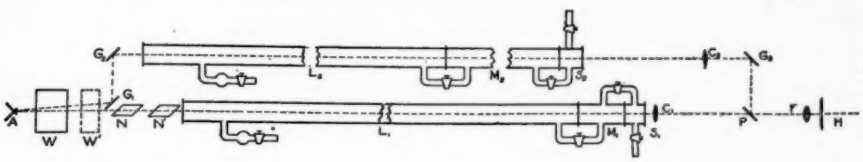

Fig. 1.

These colors were useful in preventing diffuse light when working in the blue and violet, where the spectrum was naturally faint and the absorption strong.

From W' one beam of light passed through nicol N, which could be rotated to any desired angle by a shaft running to the other end of the apparatus. The angle was determined by a scale on its mounting. From N the beam passed through a fixed nicol, N' and three tubes, L_1, M_1, and S_1, whose lengths were 185.1, 10.14, and 5.385 cm. respectively, making the expansion ratio

$$(S_1 + M_1)/S_1 = 2.88,$$

and

$$(S_1 + M_1 + L_1)/S_1 = 37.2.$$

Another beam, after reflection from the mirrors G_1 and G_2, passed through the tubes L_2, M_2, and S_2, whose lengths were 141.4, 55.30, and 5.18 cm. respectively, making the expansion ratios 11.7 and 39.0.

Mirror G_3 reflected this second beam to mirror P which reflected it parallel to the first beam, that passed over the edge of P.

While G_1, G_2, and G_3 were of ordinary silvered plate glass, P was a small piece of glass that had been scratched across one surface, covered on the other with a cathode deposit of platinum, and broken along the scratch. This process gives a plane, reflecting surface, with no appreciable rounding off of the edge, though several trials may be necessary to obtain good results. This simple and ingenious photometer, for which

I am indebted to Dr. A. H. Pfund, may also be made of silvered glass, though platinum is better if there are ever any acid fumes in the air.

The two beams, after leaving P passed through the short focus lens, F, which formed an image of the edge of P across the slit, H, of a Hilger wave-length spectrometer. C_1 and C_2 were long focus lenses used to condense the beams slightly, to give more light and avoid trouble from shadows of dust particles on the windows of the tubes.

This arrangement gave two spectra, one from each tube, and one directly over the other. Thus if the edge of P was perfect, one might focus F for any color so as to leave no black line between the spectra. I could then make their intensities equal for that color by turning the nicol, N, and my assistant, Mr. R. S. C. King, could read the angle, θ, from the position of total extinction. Since the intensity of the light transmitted varies as $\sin^2 \theta$, this gives a means of calculating the percentage chance of either beam when the condition of the bromine through which it passed was changed.

Experimental Procedure.—First the tubes were pumped to a pressure of a few cm., and bromine vapor was admitted to drive out any air in them or in the bromine reservoir, which was connected by glass only to the inlets of S_1 and S_2. Then they were pumped to a pressure of .02 or .01 mm. or less by a Gaede mercury pump protected by a hard glass tube full of hot copper gauze.

S_2 was then filled with bromine and the photometer was read. Then S_1 was filled and the photometer was read again. These readings gave the fraction of the light absorbed by S_1. (A reading with no bromine was not taken because of the excessive brightness of the light under those conditions.)

The third and fourth readings were taken with the bromine from S_1 expanded to M_1 and L_1 respectively, and the fifth and sixth with the bromine from S_2 expanded into M_2 and L_2. From the $\sin^2$ law the changes in the fraction of the light transmitted in each case could readily be determined.

The initial pressure of the bromine was determined from the temperature of the bromine reservoir and the data on its vapor tensions in Landolt & Bornstein's stable, with graphical interpolation where it was necessary. The room temperature was between 19 and 21° in nearly all the experiments.

Experimental Errors.—Treating the sources of error in the order in which we meet them in following the beams through the tubes, we have first the chance of a lack of constancy in the ratio of intensities of the beams as they leave the arc, due to a change of the position of the crater

of the positive carbon. As the angle between the beams was small, such errors could be only slight ones; and as the changes were slow, the assistant, King, could keep watch of the arc and prevent them.

The scale on the rotating nicol was tested and found accurate.

A possible source of error in photometric work of this sort with nicols is any lack of uniformity in the beam due to inaccuracies in the interface of the rotating nicol, that produce light and dark streaks in the beam that rotate with it. Fortunately, however, such errors could be avoided by inclining the axis of the nicol very slightly to the direction of the beam, though not enough to impair the complete polarization of the light.

Leaks in the stopcocks were very effectively prevented by greasing them with a stiff paste of powdered Acheson graphite moistened with pure concentrated sulphuric acid, and protected from the moisture of the air by vaseline. This combination was found much more effective than phosphoric acid, and less likely to dissolve bromine and release it again when the pressure is reduced.

Any lack of equality in the ratios of the volumes of S_1, M_1 and L_1 or S_2, M_2 and L_2 to their lengths was avoided by weighing the tubes empty and full of distilled water (which gives no air bubbles) and correcting deficiences of volume by bulbs in their outlets or excesses by bits of glass rod. These ratios were made equal to 0.1 per cent.

Except for the uncertainty of all photometric balancing, the largest error was probably due to the reflection of light from the second windows of the short tubes back to the first and then back on its original course. This might change the intensity on expanding the bromine out of the short tubes by 0.6 per cent. at most, and thereby produce an error that is present in every experiment on absorption that involves the use of such windows.

Errors due to the reflection of light from the sides of the tubes were avoided by the use of eight, slightly ground, black glass diaframs in each tube, held in place by glass braces. These of course were in the tubes when the volumes were measured.

The bromine used was obtained from the Baker & Adamson Co., and was free from all volatile impurities except a trace of chlorine, which must certainly have been eliminated by evaporation in the preliminary experiments of getting the apparatus in running order. Traces of air in the vapor, which probably would affect the result but little, were avoided by letting a large amount of vapor pass through the apparatus during the pumping to drive the air out of the reservoir and tubes, and then pumping to about .01 mm. The possibility of impurities from the de Khotinsky cement on the windows was avoided by putting all the

cement on the outside of the tubes, and letting none come through the cracks between the tubes and the windows, thus minimizing the area of cement surface exposed to the bromine.

The errors of photometric balancing were minimized by making at least four or five, and often ten, settings of the photometer for each angle to be determined, and making the intensity of the spectra uniform for as large a distance as possible above and below the line between them. A check on all these errors was furnished by the equality of the reading with the bromine in the two long tubes to that with it in the two short tubes, since the beams were absorbed equally in both these cases.

The result of all these possibilities for error is an uncertainty in the intensity of the light transmitted by the bromine which is probably not over 1 per cent. in all parts of the spectrum where the absorption is continuous; in the narrow bands, where some fine lines are visible and the intensity changes rapidly along the spectrum, the errors are much greater, though probably not over 3 or 4 per cent.

Results of Experiments on Bromine.—Satisfactory experiments were performed at ten points in the wide band, most of them being tested two or three times, and all but two of them with bromine enough to transmit less than .15 of the light of the wave-length in question. Diffuse red or yellow light was eliminated by a color screen throughout these experiments.

The wave-lengths in millimicrons, temperatures of the bromine reservoir, and initial pressures in millimeters are given in the following table:

Wave-length:	420,	430,	440,	450,	460,	465,	475,	490,	500,	507.
Temperature:	−30,	−20,	−17,	−18,	−20,	−20,	−10,	−7.3,	0,	0
Pressure:			20,				35,	45,	65,	65.

The pressures not given are for temperatures below the lowest for which Landolt and Börnstein give data. At − 20° the pressure is probably about 15 mm. The room temperature was about 20°.

From these pressures it was found that *at all these wave-lengths, with an expansion in any ratio less than 39 from the pressures given above, no change of intensity could be observed.*

This result may be stated better in terms of the absorption coefficient. If the intensity I of the light after travelling a distance x through the bromine at a density ρ is expressed in terms of the initial intensity I_0 by the equation,

$$I = I_0 e^{-a\rho x},$$

Lambert's law is that a is independent of x for any constant value of ρ, and Beer's is that a is independent of x or ρ for any constant value of the product ρx. Some approximate values of $a\rho$ at 20° and a pressure of 45 mm. (that of the triple point, − 7.3°) are as follows:

Wave-length in $\mu\mu$:	420,	440,	460,	480,	490,	500,	507.
$a\rho$ in cm.$^{-1}$:	.9,	.85,	.75,	.6,	.55,	.50,	.45.

As these values are calculated from experiments in which the pressures were not known accurately, they are not exact.

Since Lambert's law may be expected to hold for such a continuous band as this, we may express deviations from Beer's law best in terms of the relative change,

$$\frac{\Delta a}{a} = \frac{\Delta I}{I \log I/I_0}.$$

In these experiments, except at 420$\mu\mu$, where $I/I_0 = .56$, and 460, where $I/I_0 = .32$, this ratio was well below .2 and often below .1, so that its logarithm was below -1.6 or -2.3. Therefore, since I is measured to 1 per cent., we may safely say that *with expansion ratios up to 39 from the pressures quoted above, any changes in a that occur with ρx constant must be less than $\frac{1}{2}$ per cent.*

A striking contrast to this result is presented by the narrow bands, that lie on the long wave side of 510$\mu\mu$. In this region it is of little use to express the results in terms of a, for when the bands are made up of lines, and only averaged intensities over several lines may be measured, Lambert's law may be expected not to hold.

This assertion was verified by measurements of the absorption produced by different known amounts of bromine, both for a wave-length, 4,900 A, well removed from the narrow bands, and for another, 5,320 A, in a band about 20 A wide, that showed marked deviations from Beer's law. This was done by balancing the photometer first with no bromine in the tubes, again after filling and expanding S_2, a third time after filling and expanding S_1, a fourth after a second filling and expanding of S_2, and so on until the light was too faint to go farther. From the equation

$$I = I_0 e^{-a\rho x},$$

assuming Beer's law and allowing for the amount of bromine that remained in the short tubes after each expansion, the value of a for the bromine at its initial density was calculated from each measurement.

At 4,900 A, starting with a very intense light and an initial pressure of 18 mm. (temperature of reservoir, -17.5), it was found possible to fill the tubes five times, ending with tube 2 transmitting only .00375 of the light, and tube 1, on account of its slightly greater length, only .00350. At 5,320 A, with an initial pressure of 60 mm. (temperature, $-1°$) such faint lights could not be measured as well on account of the rapid variations of the intensity along the spectrum, so the tubes were filled only three times, and the fractions of the light transmitted at the end were .068 and .059.

Averaging the values of $a\rho$ from the two tubes, we have for the five steps at 4,900, the following results:

.217, .219, .221, .223, .225 cm^{-1}.

The three determinations at 5,320 gives the values:

.232, .197, .178 cm^{-1}.

The apparent change of a at 4,900 A is undoubtedly due to a warming of the reservoir, from -18.0 to $-17.0°$, which occurred during the experiment, and which would just account for this change if a is really constant. In the other experiment, no such temperature change occurred, so that the change in a at 5,320 A, which is in the opposite direction to that which would be caused by the deviation from Beer's law, is certainly due to the discontinuous nature of the narrow band.

An important result of this deviation from Lambert's law is the fact that, just as the values of a for any value of ρ depend on the length of the tube used in the experiments, the deviations from Beer's law must likewise depend on this arbitrary length.

The exact values of these deviations are therefore of no real importance, though their order of magnitude is of some theoretical interest. Since they are caused by the changes of width of the fine lines when the pressure changes, the exact widths of these lines under different pressures would be even more interesting. These, however, can be measured only with a high dispersion.

The changes of intensity of these bands often amount to 25 or even 50 per cent., as one may readily see from the graphs in figure 2, where the results of some of these experiments are shown. Other experiments at these wave-lengths and at 5,255, 5,380, 5,565, 5,665, and 5,875 A gave similar results; the general nature of the changes in all these bands is the same, as one may readily see in the spectroscope, where the whole narrow band region becomes brighter and the bands themselves slightly less distinct at every expansion of the bromine.

Experiments on Chlorine.—These experiments were performed with an apparatus similar to that used for bromine, except that the short tubes were 10 cm. long and the expansion was in one stage only, and to obtain more light in the blue and violet a spectrometer of lower dispersion was used.

Since the chlorine band lies mostly in the ultraviolet, Beer's law could be tested for only a very limited part of it. Experiments were tried on the region from 416 to 422$\mu\mu$, where intensity was increased by bright lines in the arc spectrum, that could be made to appear continuous by widening the spectrometer slit, and also for the region 435 to 437$\mu\mu$.

For longer wave-lengths the absorption was too weak to give any accuracy, and for shorter ones the spectrum was too faint. At 420, seven satisfactory experiments were performed, with initial pressures from 21 to 91 cm.; at 436 there were four, with initial pressures from 50 to 79.5 cm.

Beside the expansion experiments, others were tried on the effect of admitting dried air to the tubes containing the chlorine after the expansion. These results were not so accurate as those of the expansion experiments, because the chlorine was driven to the end of the tube by the air, and, being heavy, had a tendency to sink to the bottom of the

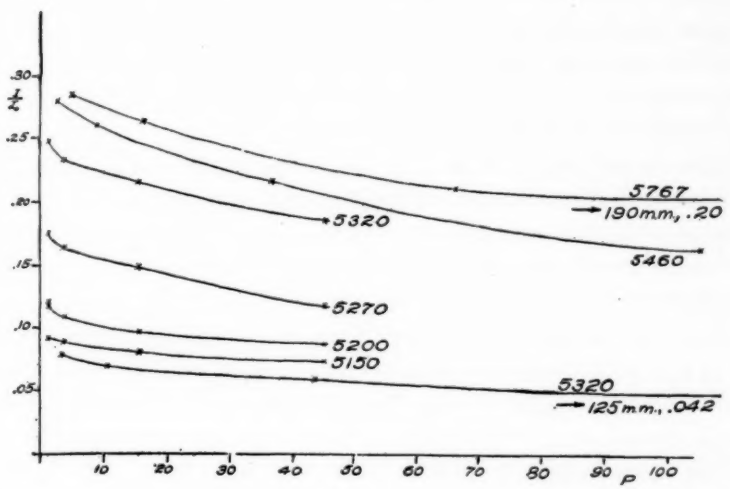

Fig. 2.

tube and thus escape from the path of the light. Such experiments could not be performed with bromine, because it would condense on the walls of the tubes and take a long time to evaporate and diffuse through the air.

At 420, the mean of all the values of $(-\Delta a/a)$ for these expansion experiments is .012, with a mean error of .004, showing an increase of absorptive power with pressure in this case. The mean of the values of $(\Delta a_a/a)$, the relative change on admitting air, is $-$ .005, with a mean error of .01, so that we cannot say that there is any change in a when the total pressure is raised by admitting air.

At 436, the mean of the values of $(-\Delta a/a)$ is $-$ .0005, with a mean error of .004; and the mean of $(\Delta a_a/a)$ is $-$ .004, with a mean error of .002, whose smallness is probably accidental. We cannot therefore say that there is any change at this wave-length in either case.

This difference between the effects at two points so near each other is quite surprising, especially as no such effects were found in bromine.

An explanation, however, is suggested by the experiments of M. Trautz,[1] who finds that light absorbed in chlorine produces not only the well known increase in its chemical activity, and the Budde effect, or sudden expansion of 10 or 12 per cent., but also a sudden drop of several per cent. in its specific heat at constant volume, with a corresponding rise in the specific heat ratio. All these effects are reversed at once when the light is shut off. These phenomena indicate that the light probably produces some allotropic modification of the chlorine, just as light of the Schumann region converts oxygen to ozone.

As this reaction causes a change of volume, and as it is reversible, any expansion must cause a change in the percentage of the unstable form. Thus if the unstable form has an absorption band different from that of the unmodified chlorine, there will be deviations from Beer's law that will be different for different parts of the band.

In this connection it may be noted that the addition of air, unlike compression, does not increase the frequency of collisions of the chlorine molecules, and thus promote the reversal of the reaction caused by the light. It is therefore not surprising if the addition of air does not reverse the optical effect of the expansion.

Summary of Results.—A rapid increase of absorptive power of a given mass of gas with pressure was found by Janssen in the visible bands of oxygen, and by Ångström, von Bahr and others in the infra-red bands of many gases.

In the wide band of bromine, these experiments show that such changes, if they exist, must be extremely small; the slight change found in chlorine, due possibly to chemical effects, is very small compared to those in oxygen or the infra-red bands.

The narrow bands of bromine, like those of the infra-red, show a rapid increase of absorptive power with pressure. The effect in this case seems to be due to the widening of the fine lines composing these bands.

PART II. THEORETICAL.

This part of the paper contains a brief critical review of the development of the theory of absorption to its present state, with special reference to its explanation of pressure-absorption effects and some suggestions as to how the theory may be modified to give a better account of such phenomena. It is then shown how this modification helps in the explanation of some other phenomena of absorption.

The first explanation of the difference between the dielectric constant and the square of the index of refraction of any substance as a result of

[1] Z. fur Elektrochemie, *18*, 513–20, 1912, or see A. Reis, Die Naturwissenschaften, *1*, 38, 1913.

the inertia of minute charged particles in it was given by Maxwell,[1] but was forgotten until resurrected by Rayleigh in 1899. Meanwhile an elastic solid form of it had been re-invented by Sellmeier and developed by Helmholtz and Ketteler into something like the present electromagnetic form.

The fundamental assumption on which this theory in its present form is based is that the electrons are free to vibrate about certain positions of stable equilibrium. Since the existence of nearly monochromatic radiations suggests that these vibrations are simple harmonic, it is often assumed that the restoring force on the electron is approximately proportional to its displacement from its equilibrium position, and sometimes that it is due to a continuous distribution of positive electricity through which the electron moves.

A well-known result of this hypothesis is that, when subject to a sinusoidal electric force, the electrons will execute steady vibrations about their positions of equilibrium with amplitudes depending not only on the maximum value of the force, but also on the frequencies of the force and of the electrons' own free vibrations. Thus the polarization of the medium, and consequently the index of refraction, μ, will depend on the frequency according to the well-known equation,

$$\frac{4\pi P}{E} = \mu^2 - 1 = \frac{4\pi Ne^2}{m(n_0^2 - n^2)},$$

where P is the polarization, measured in the standard electrostatic system, E the electric force, whose frequency is n, m the mass of the electron, e its charge, and N the number of vibrating electrons per unit volume. n_0, the frequency of the free vibrations of the electrons, is always the frequency of an emission or absorption band. This formula for the dependence of μ on n and n_0 agrees well with experimental results.[2]

The dependence of μ on N, and consequently on the density of the absorbing gas, has been treated very successfully by Lorentz,[3] by a slight modification of this formula, taking account of the influence of surrounding molecules on the vibrations of the one in question, on which they exert an electrostatic force equal to aP, where a is a numerical constant, approximately $4\pi/3$. Since $P = Ner$, this results in a ponderomotive force aNe^2r, acting against the restoring force, and thereby weakening the resultant of the two by a very small amount proportional to N. Thus in the above formula for μ, the frequency n_0 of the free vibration of a single electron must be replaced by the slightly lower frequency,

[1] Math. Tripos Exam., 1869.

[2] See, for example, D. A. Goldhammer, Dispersion und Absorption des Lichtes, B. G. Teubner, 1913.

[3] H. A. Lorentz, Theory of Electrons, B. G. Teubner, 1909.

$$n_0' = \sqrt{n_0^2 - \frac{aNe^2}{m}},$$

with which a large collection of these electrons would vibrate freely in unison.

For the effect of increasing density on absorption lines, this gives the well-known shift toward the lower frequencies; and for the effect of density changes on μ it gives the formula,

$$\frac{\mu^2 - 1}{\mu^2 + 2} = constant \times \text{density},$$

which was found by Lorentz to agree well with Lorenz's experiments.

This theory would lead one to expect a steady vibration of each electron, in phase with the inducing force if $n < n_0'$, in opposite phase if $n > n_0'$, and of an amplitude becoming infinite as n approaches n_0' from either side. Since this last result is evidently absurd, some additional assumption must be made to avoid it. So far all theories of absorption based on the classical electromagnetics agree, but in this assumption they differ.

A way out of this difficulty appeared to Planck to be the assumption that the electron was restrained enough by the force $(2/3)(e^2/c^3)(d^3r/dt^3)$, which results, along with the force of inertia, $-m(d^2r/dt^2)$, from the effect of the radiations from each part of the electron on other parts, and which accounts for the damping of vibrations by radiation.

This force, however, is so small that when $n = n_0'$, according to Wood, the vibration would attain such an amplitude that with only one electron in a cube a wave-length on an edge the intensity of the light would be reduced to one half in going a single wave-length.

Furthermore, with so few vibrating electrons, we run into still another difficulty, because in deriving the equations of propagation of light through systems of molecules, the electric and magnetic vectors were averaged over volume elements that were small compared to distances in which appreciable changes occur, but large compared to distances between molecules. In this case, such elements do not exist, and the problem must be treated by considering the forces radiated from each electron separately.

In the direction of the beam these forces would result in weakening the original force; and in other directions they would cancel each other only if there were many electrons in each cube a wave-length on an edge and if the intensity changed but little within a wave-length. These two conditions, as we have seen, are mutually inconsistent if the electrons are retarded only by their own radiations. If, nevertheless, these con-

ditions are not satisfied, the radiated forces will not cancel, and there will be a strong resonance radiation, or selective reflection.

Thus it appears that this is not really a theory of absorption at all, but of reflection only, so that we may expect it to approximate to the truth only in cases, such as in mercury vapor at wave-length 2,536 A and the sodium D lines as observed by Wood, in the light of comets' tails, at the surfaces of solid aniline dyes, and in other such cases where strong selective reflection occurs. The more completely the light is reflected, rather than absorbed, the larger part of the damping of the vibrations may be assigned to this cause. But where there is any true absorption, there must be some other retarding force as well.

Perhaps the most natural assumption to obtain this force was the one made by Helmholtz, that the electron moves in a viscous medium, with a resistance proportional to its velocity. This hypothesis, nevertheless, has many serious disadvantages, the greatest of which is that it neglects the most obvious experimental fact in the whole subject of absorption, namely the heating of absorbing substances by light. For in ordinary bodies, friction, which we explain by molecular collisions, always transfers energy from the larger bodies to the molecules, whose heat motions are thereby strengthened; but no amount of friction within an isolated mechanical system ever produces motion of the system as a whole. Similarly this electronic friction would transfer energy from the electrons to some sort of sub-electronic bodies, from which it could not all be recovered, and thus it would violate the law of the conservation of observable energy; likewise it would never transfer energy to the molecules, which do, as a matter of fact, acquire it.

Lorentz, recognizing this defect in Helmholtz's hypothesis, and also wishing to account for the widening of absorption lines by pressure, assumed that there was no damping, but that the electron could continue to vibrate further and further, restrained only by radiation, until the molecule collides with another. Then, he assumed, all the energy of the vibration would be transferred to energy of translation of the molecules. The effect of this he proved equivalent to a damping force, $-g(dr/dt)$, where $g = (2m/\tau)$, τ being the mean time between collisions of a molecule. Thus, defining the absorption coefficient k by the equation

$$I = I_0 e^{-kz}$$

and denoting its maximum value by k_m, one may prove that

$$k = \frac{4\pi n^2 g N e^2/c}{m^2(n_0'^2 - n^2)^2 + n^2 g^2}, \quad k_m = \frac{4\pi N e^2}{cg}, \quad \frac{k}{k_m} = \frac{1}{1 + \frac{m^2}{n^2 g^2}(n_0'^2 - n^2)^2}.$$

Thus one may evaluate τ from data on the width of an absorption line, which Lorentz defines as the frequency interval from n_0' to a point on either side where $k/k_m = 1/\kappa$, κ being some small number, say 10 or 20. For this position $\tau(n_0 - n) = \sqrt{\kappa - 1}$. Hence as the pressure increases, and τ decreases, a line must widen, though the absorption at the center must decrease, these effects being just what Dufour[1] found in nitric peroxide and bromine on adding air.

On evaluating τ from this equation, with Hallo's statement that the D lines in a certain sodium flame were an Ångström in width, Lorentz found τ of the order of 1 or 2 times 10^{-11} sec., whereas the kinetic theory would give 10^{-10}. Yet these lines were narrow compared to the oxygen and halogen bands, and to the ultra-violet bands of all gases.

As a better explanation of the wide bands, Livens[2] called attention to an omission in Lorentz's treatment of the influence of the surrounding molecules on the vibrations of an electron. In evaluating the factor a of the electric force aP, Lorentz divided these electrons into two classes, the first including all that lie outside of a sphere drawn around the electron in question with a radius large compared to the distance between molecules, but small compared to the wave-length, and the second including all within this sphere. The force due to the first class was proved to be $(4\pi/3)P$, while that due to the second would be zero if the molecules were in a regular cubical arrangement, so it was taken as zero for the haphazard arrangements found in a gas. But as Livens pointed out, even though the mean of all its values for all the molecules in a gas is zero, it is rarely zero for any individual molecule, because of the lack of symmetry of the surrounding ones, though it may be either positive or negative. Hence the modified frequencies of the electrons would not all equal n_0', but some would be greater and some less. Thus as the line shifted with pressure, it would also widen.

As Livens said, this would account not only for pressure widening of lines in gases, but also for the comparatively great width of bands in solids and liquids.

A critical examination nevertheless shows some serious defects in Livens's theory. In the first place, he abandons entirely Lorentz's assumption of damping by collisions, which is necessary in some form to account for heating by light without ionization or chemical change; and he assumes Helmholtz's internal friction, which is impossible, not only for the reasons noted above, but also for many others, such as the fact that it would not allow resonance radiation in extremely rarified gases, nor ionization in the ultra-violet by feeble intensities of light.

[1] L. c.

[2] Phil. Mag., *24*, 268–93 and 523–8, 1912.

Furthermore, on Livens's theory the width of a band in a liquid or solid might be expected to increase with the number and electric moment of the molecules vibrating in phase with the one in question. Thus we should expect wide deviations from Beer's law in solutions, though it is well-known that in the absence of chemical changes such deviations do not occur.

Finally, for similar reasons, we should not expect much difference in the widths of bands of about the same intensity in different solutions, though those in crystals might differ. Livens's effect therefore can account only for the width of the narrowest bands observed in solutions, that is, for widths of a few Ångströms observed in the salts of the rare earths. Wider bands, in solutions, and especially in gases, are still unexplained.

Even the Doppler effect, which has often been invoked to explain part of the width of lines in gases, has been found guilty of only a small fraction of an Ångström.

Unequal Frequencies of Free Vibration in a Band.—Collecting the possible sources of width in a band, and the widths for which they can account, in gases, we have: first the damping by radiation, giving possibly a few thousandths of an Ångström; second, damping by collisions, giving perhaps a few tenths; third, the Doppler effect, ordinarily negligible; and fourth, Livens's effect, giving perhaps a few tenths. All these causes together would probably not give over an Ångström under the most favorable conditions, and the bands to be explained range from a few thousandths of an Ångström to hundreds in width.

We are therefore driven to the assumption that *the natural frequencies of the electrons, when free from all electrostatic influences of their neighbors, are not so nearly equal as they are ordinarily supposed to be.*

This assumption is not entirely new, since the statement that some bands are made up of fine lines is a form of it in which the different frequencies are separated by finite intervals. This suggests the possibility that all bands over about an Ångström in width may be composed of fine lines, just as the narrow bands of bromine are.

In deciding this point, tests of Beer's law are of especial value. For unless the distances between the centers of the lines are much less than the widths of the lines themselves, they ought to give deviations from Beer's law with any dispersion too low to resolve them. Therefore, although other causes, such as changes in the number of absorbing molecules, may also given deviations from Beer's law, a band that obeys it may probably be assumed to be continuous.

From the experiments described in the first part of this paper, *that*

show great exactness for Beer's law as applied to the wide band of bromine, and deviations in chlorine that are very small and that may be due to chemical changes, we may now conclude that *the width of these bands is probably due to a continuous distribution of frequencies of undisturbed vibrations.*

In sharp contrast to these results are those of Janssen in the visible oxygen bands and Ångström and von Bahr in the infra-red bands of many gases, where large deviations from Beer's law were found. In some of the bands investigated by von Bahr, signs of discontinuity were discovered, both during these experiments and later[1] with a higher dispersion. In some cases, however, the absorption seemed to increase with pressure even after the lines had widened into a perfectly continuous band, as though the increased pressure kept a larger fraction of the molecules in a condition for absorption.

Consequences of the Hypothesis of a Continuous Distribution of Free Frequencies.—Inquiring as to the cause of this distribution of free frequencies, we are met by the question of the origin of the restoring force that was assumed in explaining the elementary facts of absorption. Except in the infra-red, where the vibrations are probably those of charged atoms, it may, as has usually been supposed, be due to a sphere of positive electricity in which the electron moves, or it may be explainable only by the quantum hypothesis. Since, however, the latter hypothesis gives as yet no explanation of pressure-absorption effects, we may disregard it here.

On the positive sphere hypothesis, if there are several electrons in an atom, the force on any one of them when it is displaced a given distance from its position of equilibrium will be modified by any change in the positions of the others, or by any compression or distortion of the sphere such as chemical and cohesive forces would produce. It would therefore be really quite surprising if the frequency of any electron or group of electrons were always exactly its normal value, and it is reasonable to suppose that it may often be subject to great deviations from this value. Similarly in the infra-red, the frequencies of vibrating atoms must be modified by any intra-atomic motions such as would be caused by collisions.

From these considerations it is evident that an increase in the violence of the collisions will increase such disturbances and therefore widen the lines or bands. This is confirmed experimentally by the widening of the infra-red bands examined by von Bahr, and also of many finer visible lines, by a rise of temperature.

[1] E. v. Bahr, Deutsch. Phys. Ges., Verh. *15*, 16, pp. 710–737, and *15*, 21, 1150–58; A. Eucken, ibid., pp. 1159–62.

Similarly the strong and very irregular cohesive forces and pressures that are put upon the atoms in liquefaction may be expected to produce the wide and perfectly continuous bands that are observed in most liquids and solids.

Since the wide bands of bromine and chlorine do not seem to be affected much by a change in the frequency of collisions, it appears that they, and probably the similar bands found in other gases in the ultra-violet, must owe their width to intra-molecular motions that are not much affected by collisions.

Heating, Ionizing and Chemical Effects of Absorption.—The fact that these bands do not behave like those of the infra-red may, in the light of our new assumption, be closely related to the fact that absorption of light of low frequencies results only in heat, while that of high frequencies is much more likely to produce ionization or chemical effects. For now that we are free to follow Lorentz in ascribing the damping of the vibrations to collisions, we may well inquire why such a damping should occur. Since the collisions at ordinary temperatures do not set electrons of visible frequencies into an appreciable state of vibration, they cannot be sudden shocks, but must involve gradually increasing and decreasing forces, that last for several periods of such vibrations. Conversely, since the maximum energy density in the black body spectrum at ordinary temperatures is near 8 or 9 μ, we may expect the times of collisions to be of the order of magnitude of a single period of vibration of such light, that is, about 10 or 20 periods of visible light.

If now two molecules collide with a low frequency electron or atom in a state of violent vibration, it may be expected to transfer some part, though not necessarily all, of its energy to the translatory motion of the molecules. If, on the other hand, the frequency is high, it will execute many vibrations during the collision, and any forces on the other atom due to it will alternate so many times during their approach and recession that they will produce no change in the energy of translation. Thus we may expect the production of heat readily by low frequencies, but not so readily by high.

This being the case, the energy of high frequency vibrations will accumulate without much molestation by collisions even in a solid; likewise, if the collisions occur very seldom, as in the tail of a comet, where the molecules are about a meter apart, we must have an undisturbed accumulation of energy of any frequency.

This process may give various results. First, if the electron is bound firmly enough, it will accumulate energy until it reaches the limit set by the damping by radiation, and then it will continue to emit the strong

selective reflection observed in comets' tails and in sodium and mercury vapors.

If however such an amplitude of vibration would cause the electron to escape from the atom, then ions will be produced in a gas or photo-electrons from a solid. Here it may be noted that, in the absence of any considerable damping, such ionization will occur even with very low intensities, though greater intensities will produce ions quicker, and consequently more often. Likewise, since ionization occurs as soon as a certain amplitude is reached, the subsequent velocity of the electron will not depend at all on the intensity of the light.

Still another possibility in such cases is that the electron will be thrown into some other situation in the atom by its vibration, and thereby change its chemical behavior, thus producing the well-known stimulation of reactions, especially of decomposition, by light.

SUMMARY.

1. A critical analysis of Helmholtz's assumption of viscous resistance to the motion of a vibrating electron shows that it is inconsistent with experimental facts, and that Lorentz's hypothesis of damping by collisions is necessary to account for the production of heat by light of low frequencies.

2. A compilation of the possible causes of width of spectrum lines then shows a deficiency in the present theories that can be remedied best, as shown by the experiments on chlorine and bromine, by the assumption that the frequencies of free vibration of electrons producing a band are not all equal, but are often continuously distributed about their normal value.

3. This assumption is found to lead to an explanation of the production of heat by low frequencies, of ionization and chemical effects by high, and of the strong selective reflection observed in comets' tails and other extremely rarified gases. Finally, the laws by which chemical effects and ionization depend on the intensity of the light are explained.

ON THE ASYMMETRIC EMISSION OF PHOTO-ELECTRONS FROM THIN FILMS OF PLATINUM. I.

By Otto Stuhlmann, Jr.

Introduction.

As early as 1889, W. Hallwachs[1] showed that a photo-electric effect could be obtained from a silvered quartz plate when light was incident through the quartz.

Later Rubens and E. Ladenburg[2] took up the work and observed a similar effect for gold leaf. They found the ratio of the photo-electric effect for incident and emergent light to be 100 to unity while the fraction of the ultra-violet light transmitted, photo-electrically measured, was one one-thousandth of the incident.

The work was taken up by the writer[3] who showed that the photo-electric effect of thin cathode films of different metals deposited on quartz depends on the thickness of the film and whether the film is on the side of the quartz facing the light (incident effect = I) or on the side away from the light (emergent effect = E). The ionization currents were measured in air. It was shown that when the films are thin enough, about 10^{-7} cm. or less, that the ratio emergent to incident currents (E/I) was greater than unity and for thicker films less than unity. This ratio was constant for thin films and was shown to be equal to 1.17 for platinum.

Independent experiments carried out by R. D. Kleeman[4] both in hydrogen and in vacuo led to the same conclusion as to the asymmetry of the photo-electric effect for emergent and incident light.

Recently J. Robinson[5] showed that the above observed dissymmetry of emission should be separated into two quite distinct effects; the actual number of electrons emitted and the velocities of the electrons emitted.

As to the Actual Number of the Electrons Emitted.

It was shown by Robinson[6] that the magnitude of the ratio of emergent to incident current depended upon the source of illumination. When the

[1] W. Hallwachs, Tagebl. d. Heidelberger Nat.-Vers., S. 24, 1889.
[2] Rubens and E. Ladenburg, Ber. d. D. Ges., 24, p. 749, 1907.
[3] O. Stuhlmann, Jr., Phil. Mag., 23, p. 854, 1911.
[4] R. D. Kleeman, Proc. Roy. Soc., 84, p. 92, 1910.
[5] J. Robinson, Phil. Mag., 23, p. 542, 1912. Pt. II., Phil. Mag., 25, p. 115, 1913.
[6] Loc. cit., Pt. II., p. 125.

films were illuminated by a spark between brass terminals the ratio of emergent to incident effect was equal to 1.27, while a mercury vapor arc in quartz changed the value to 1.16. An iron arc as originally used by the writer gave 1.17 for this ratio. More recent results show a change in this value in a decreasing order of magnitude as follows: iron arc, quartz mercury vapor lamp, iron spark, zinc spark and cadmium spark in air.

The current curves plotted against film thickness show a maximum at about 10^{-7} cm. For thin films the emergent being greater than the incident effect. The rate of increase, however, does not take place so suddenly as Robinson's curves lead one to think. A more careful study of the change of current with film thickness as shown by the writer and K. T. Compton,[1] attributes the sudden tremendous increase in current, to method of making contact between film and holder when the plates are sputtered in vacuo.

Recently Partzsh and W. Hallwachs[2] became interested in this question from an optical point of view. They investigated a series of cathode deposited platinum films ranging in thickness from 1 to 50$\mu\mu$. The incident, reflected and transmitted beams were measured both for emergent and incident positions. If the film were illuminated so that the transition layer was quartz-platinum, 40 per cent. more light was absorbed by the film than when the illumination fell directly on the metal side. They further showed that the reflection coefficient for the transition layer quartz-platinum, at first decreased with increasing thickness of film to about 3$\mu\mu$ where a minimum occurred. Then increased until at 7$\mu\mu$ the original value recurred. A further increase in thickness was accompanied by an increase in the reflection coefficient until it approached the value for platinum. From these data in connection with the values of the variations in transmission with change in thickness of film one may plot the absorption curve.

Since absorption of light and photo-electric current are proportional, one would expect these curves to be identical with the ones obtained by measuring the photo-electric current with change in thickness.[3] This, however, is not quite true, because the photo-electric effect shows a peculiar sudden[4] increase in current and then a well-defined minimum, which the curves by Partzsh and Hallwachs do not account for.

They further show that thin platinum films on quartz, whose thickness is less than 10^{-6} cm., absorb, when illuminated through the quartz plate,

[1] O. Stuhlmann, Jr., and K. T. Compton, PHYS. REV., S. 2, Vol. II., p. 205, 1913. Pt. II., PHYS. REV., S. 2, Vol. II., p. 327, 1913.

[2] Partzsch and W. Hallwachs, Ann. d. Phys., 41, p. 247, 1913.

[3] Stuhlmann and Compton, PHYS. REV., S. 2, Vol. II., p. 208, 1913.

[4] For a possible explanation of this see J. Robinson, Phil. Mag., 25, p. 127, 1913.

1.5 to 1.4 times as much of the incident light as when the illumination falls directly on the platinum. These differences, the authors conclude, are great enough to account for the ratio of the emergent to the incident effect as photo-electrically measured by Kleeman, Robinson and the writer.

It was thought by some writers, since the ratio of the emergent to the incident effect was greater than unity, that the emitted electrons received a velocity component in the direction of the propagation of the light. A longitudinal action of the light, if present, is evidently of a smaller order of magnitude than the above photo-electric ratios, of emergent to incident currents, seem to indicate.

As to the Velocities of the Electrons Emitted.

The maximum velocities of emission, for platinum cathode films deposited on quartz, were also investigated by J. Robinson.[1] He found that for very thin films (less than 10^{-7} cm.) the maximum velocity of emission due to the emergent light was greater than that due to the incident light; for thicker films the reverse was found to be true. In his first paper the maximum value for the ratio of emergent to incident velocities, as obtained by projecting his curve backwards, gives 1.24, while his second paper shows only 1.12 for this maximum value, although the same apparatus and source of illumination were used.

Since the maximum energies of emission are independent of the intensity of the source of illumination, Partzsh and Hallwachs[2] conclude that the variation in absorption of the two positions of the films would be no adequate explanation of this observed change in velocity.

Robinson also determined the distribution of velocity curves for four samples of platinum films of different thickness. Partzsch and Hallwachs believe that objections might be raised to these results, in so far as values for the velocities were obtained only at two volt intervals, hence making any conclusions that might be drawn from the curves doubtful.

Concerning the Velocities with which Photo-electrons are Emitted from Matter.

An interesting and valuable suggestion was recently made by Mr. A. Ll. Hughes[3] concerning the velocities with which photo-electrons are emitted from matter. In his review of the literature on the subject of emission of photo-electrons from metallic surfaces, he emphasizes the

[1] Loc. cit.

[2] Loc. cit., p. 267.

[3] A. Ll. Hughes, Phil. Mag., 25, p. 683 (1913).

fact that the maximum velocities investigated were always those of electrons emitted from the side of the plate on which the light was incident. Under these conditions the Plank constant (h) as experimentally determined by the application of the Einstein-Richardson[1] equation, for the photo-electric effect, was always found to be less than 6.55×10^{-27} ergs sec., by an amount ranging from 10 to 25 per cent. Robinson[2] in his experiments on very thin platinum films shows that the velocities of the electrons for emergent light are greater than those for incident light, for thicker films the reverse is the case. For a certain thickness of film the emergent velocity is equal to the incident velocity and special experiments showed that for the same thickness of film the emergent current is equal to the incident current. The orientation of the plane of polarization of the light did not have any influence on the dissymmetry.

It may be inferred that originally all the electrons are, perhaps, emitted more or less in the direction in which the light is traveling and that the energy lost by a photo-electron in swinging round from its original direction of emission is at least comparable to the per cent. increase of the emergent over the incident effect. For an infinitely thin film this difference as shown by Robinson is about 12 per cent. Introducing the correction suggested by the asymmetric emission, Hughes concludes that the experimental and theoretical results may be made to check in the case of platinum, and presumably in other cases also, if we keep in mind the electrons which emerge in the direction of the incident light.

H. S. Allen[3] suggests that if this be borne out by further experiments, we reach the important conclusion that for light of a given frequency, electrons acquire the same energy in the case of all metals, though the work done in escaping is a quantity characteristic of the metal.

No experimental results as to the ratios of the emergent to the incident velocities for other metals are available and so it is not possible, at present, to test this view further. More precise information would be obtained if the ratios were investigated using monochromatic light. In view of these suggestions a further study of the velocities of emission from thin metal films was warranted.

PART I.

The first part of this paper is devoted to a solution of some of these questions. With this object in view Robinson's design of apparatus was practically adopted, in order, first to determine if his results could be

[1] O. W. Richardson, PHYS. REV., Vol. 34, p. 146 (1912); Phil. Mag., 23, p. 615 (1912); Science, 36, p. 57 (1912).

[2] Loc. cit.

[3] H. S. Allen, Photo-Electricity, Longmans, Green & Co., 1913.

duplicated, second to get the distribution of velocity curves for emergent and incident effect with change in thickness of the films.

APPARATUS.

The apparatus as shown in Fig. 1 consists of a heavy brass outer cylinder put to earth. Coaxial with it is a light brass cylindrical box (C) supported by a rod passing through a ground glass stopper B. A circular quartz plate Q, 1 mm. thick and 2 cm. in diameter, passing through the ground glass stopper R and insulated from it with hard sealing wax, projects into the inner cylinder. This quartz plate is covered with the platinum deposit in the form of a semi-transparent film and is attached to the rod by means of a screw clamp. The ground glass joint served to rotate the quartz plate through any angle so that the film may be made to face the light or be turned away from the light, in order to measure the photo-electric effect in these two positions. The inner cylindrical box (C) is 7.5×3.5 cm. over all, with circular openings at both ends, 2 cm. in diameter. The cylinder was connected to a potentiometer circuit P containing a Weston standard voltmeter reading to one one-thousandth of a volt. The electrometer, connected to the quartz plate carrying the platinum film, gave a deflection of 765 divisions per volt at a scale distance of one meter.

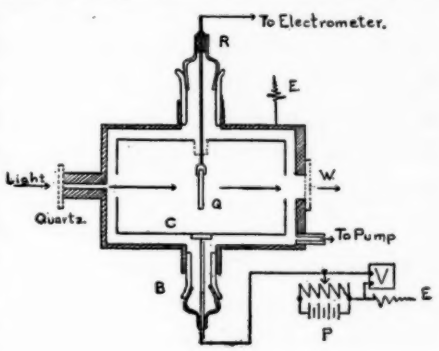

Fig. 1.

All the internal metal surfaces were covered with camphor soot to prevent effects due to stray reflected light.

A narrow beam of light from a quartz mercury vapor lamp stopped down to 3 mm., passed through a quartz lens (f 15 cm.) which focused the source on the platinum film. The beam entered the apparatus through a quartz window 1 mm. thick and passed out through a plate glass window at W. The quartz plate Q, carrying the metal film, the quartz window and the glass window at W, were all parallel and normal to the incident beam, so that any reflected light passed back along its entering path. This was obtained by rotating the plate Q until the reflected light passed through the forward opening.

The source of light was a quartz Cooper Hewitt mercury vapor lamp (Type Z) using 4 amperes direct current at 110 volts. It was found to be a reliable, very constant and brilliant source of illumination.

The platinum films were deposited from a circular platinum disk 5 cm. in diameter, in a separate glass chamber. From here they were introduced rapidly into the testing vessel. Previous experiences with these metal films having shown that such handling does not effect their photo-electric properties. Experiments by the writer and K. T. Compton[1] have shown that a cathode discharge, through the apparatus in which velocity measurements are to be made, may deposit films giving off electrons with spurious high velocities. Under these conditions the films may also show effects depending on the method of making contact between them and the holder, such results having previously been interpreted as properties of these cathode films. To insure against these effects the films were deposited in a separate chamber and mounted for examination in identical ways Through the control of the cathode fall and current Tyndall and H. G. Hughes[2] have conclusively shown that the thickness of the film is a linear function of the time.

A Gaede rotary mercury pump was used to furnish the desired vacuum. A gold leaf mercury vapor condenser was inserted just after the pump to prevent the mercury vapor from amalgamating with the platinum films. The results were all compiled from data taken at a pressure of 2×10^{-5} cm. or less.

VELOCITY MEASUREMENTS OF THE RATIOS E/I.

The maximum initial kinetic energy of the emitted electrons, expressed in equivalent volts was determined by charging the cylinder C to such a negative potential that the electrometer connected to the platinum coated plate Q, showed no deflection. The velocity v of an electron is connected with this maximum potential V by the relation $\frac{1}{2}mv^2 = eV$. The equivalent maximum potential taken up by the film was measured, when the film was turned to face the light (I) and when it was turned away from the light (E).

This maximum potential was corrected for contact difference of potential, since under the above conditions the electrons are driven back into the metal by a difference of potential equivalent to the contact difference of potential between the platinum and the surrounding metal case, plus the potential impressed by the outside circuit on the cylinder. The contact difference of potential was measured in air by means of the ionization method. For this purpose a tube containing 0.89 mg. of radium chloride was fastened against the window W and the potential measured to which the cylinder (C) had to be charged to produce no deflection. This method is very sensitive to changes in contact differ-

[1] Loc. cit.

[2] Tyndall and H. G. Hughes, Phil. Mag., 27, p. 415, 1914.

ence of potential and has been very successively used by K. T. Compton[1] and N. Shaw.[2]

It was found that very erratic results were obtained upon first introducing the films into the testing chamber. Separate experiments showed a gradual change to a steady state. This was shown to be due to the gradual drift of the contact difference of potential to its final value. For thin films this effect was more pronounced than for thicker films. The contact difference of potential rose rapidly to a maximum of several volts, from where, after several hours, it exponentially dropped to its final constant value. For very thick films or a metal plate no such maximum appeared, the curves rapidly rising to their normal value, giving identical results as those obtained by N. Shaw.[3] The following data were obtained after the steady state had been reached.

TABLE I.

Measurements of the Maximum Energy of the Electrons Produced by Incident and Emergent Light.

Relative Thickness of Film.	Emergent Light.		Incident Light.		Ratio of Emergent to Incident Energy Corrected for C.D.P.
	V. Max.	C.D.P.	V. Max.	C.D.P.	
1	.428	+.295	.212	+.298	1.42
2	1.000	.300	.565	.303	1.49
3	1.630	.254	1.667	.202	1.01
4	1.094	.322	1.224	.302	.927
5	.600	.356	.775	.337	.860
Pt. plate.	.....	.....	1.438	.353	.....

Table I. gives the ratios of emergent to incident kinetic energies corrected for contact difference of potential as obtained above. It was assumed that the measurements of contact difference in air would not differ appreciably from those measured in vacuo, under the same conditions. Characteristic results are only given, showing the variation in the ratio E/I with change in thickness. Numbers 1 and 2 are characteristic results from very thin transparent films whose thicknesses are less than 10^{-7} cm. Number 3 is quoted because of its unique value showing a film where the emergent and incident effects are practically the same. Numbers 4 and 5 show the change in the values of E and I to thick films, while the value for a freshly scraped platinum plate is given as a comparison standard.

It is evident that the films are of platinum since they possess practically the same contact difference of potential as the platinum plate.

[1] K. T. Compton, Phil. Mag., 23, p. 579, 1912.

[2] N. Shaw, Phil. Mag., 25, p. 241, 1913.

[3] N. Shaw, loc. cit.

They are consistent with previous results obtained along a different line[1] and agree with those cited by Robinson[2] except in so far as the ratios given above are a little larger. This is perhaps due to the fact that each of the above values is the mean of several determinations obtained by means of a null method of observation. They differ from Robinson's results in so far that these and previous results by the writer and K. T. Compton[3] show that a distinct maximum exists both for incident and emergent energies at a thickness comparable to 10^{-7} cm., where Robinson found his maximum for the current-thickness curves. After this maximum the emergent energy diminishes as the thickness of the film increases while the incident energy gradually increases to the normal value for platinum[4] as the thickness of the film increases. From the data of Partzsh and Hallwachs[5] one may plot the absorption curve for changes in thickness. No such pronounced maximum exists, as would account either for the sudden increase in current or velocity. The hypothesis of a longitudinal component in the light producing the asymmetry is highly improbable. The theory advanced by Robinson of a secondary effect coexisting with the liberation of an electron is one which has to be reckoned with. At any rate further information is desirable before advancing even a tentative hypothesis to explain the asymmetry in the velocity of emission.

VELOCITY DISTRIBUTION CURVES.

A curve giving the relation between the photo-electric current and the potential difference between the illuminated film and the surrounding case is called a velocity distribution curve.[6] When the potential difference is such as to retard the electrons then the photo-electric current is usually taken to be the measure of the number of electrons possessing velocities greater than that implied by the potential difference. If no contact difference of potential existed the ideal curve would saturate at zero potential.

It is well known that these velocity distribution curves are liable to distortion by reflection of electrons, but the value of the maximum velocity is not effected by them. If reflection of electrons by the surrounding case takes place the curve will be modified and depressed along

[1] O. Stuhlmann and K. T. Compton, PHYS. REV., S. 2, Vol. II., p. 205, 1913.

[2] J. Robinson, loc. cit.

[3] Loc. cit.

[4] Loc. cit.

[5] Loc. cit.

[6] For the theory of the "Velocity Distribution Curves" see A. Ll. Hughes, Phil. Trans. Roy. Soc., Lond., *A*, Vol. 212, pp. 205–226, 1912.

the current axis in proportion to this reflection, hence giving a slight negative current for potentials greater than the equivalent maximum velocity. Reflection of light also alters the shape of the curve, but this has been taken care of by blackening the interval surfaces with camphor soot. The photo-electric sensitiveness of this effect falls within the experimental errors. The effect of a stray magnetic field or of the approaching of the electrons to the surface in an oblique direction both tend to shift the curve.

With the existing apparatus experiments were made to determine how the velocity distribution curve normally obtained from solid metals under the above conditions was effected by the change in direction of the illumination on the metal film. Second to see if a change in thickness of the film was followed by a corresponding change in the slope of the curves analogous to the change in the absorption curves of Partzsch and Hallwachs. Third to determine whether the asymmetry of the maximum velocity could be substantiated by the relative magnitudes of the curves.

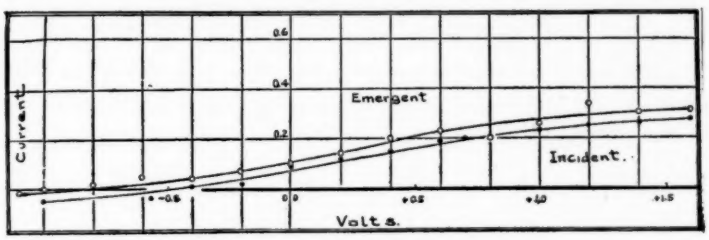

Fig. 2.

The films used were the same as those shown in Table I., for which the maximum velocities were determined. The observations were made at the same time as the previous values for the maximum velocity. The film was rotated to face the light when a definite potential difference was maintained between it and the cylinder and the speed of the electrometer index noted. The plate was then rotated through 180° so that the film was turned away from the light and the reading repeated. These readings for alternate emergent and incident effect were taken at 0.2 volt intervals. They could be checked by taking each curve separately.

The curves of Figs. 2 and 3 show this distribution of velocity among the electrons of films 1 and 2 in Table I., whose thicknesses are less than 10^{-7} cm. The ratio of the emergent to the incident effect throughout the whole range of potential is constant. This is significant in so far as it shows that the asymmetry for the maximum velocity can not be a spurious effect. This ratio can not be affected by any of the errors discussed above. If the emergent and incident curves are modified by the errors,

they will be equally affected, so that they will not influence the ratio E/I. The measurable currents are small so that the individual readings are susceptible to errors. Several readings were taken, for each point on the curves in order to reduce the average deviation to about 3 per cent. At any potential the number of electrons emitted for the emergent position are greater then the number from the incident position. This

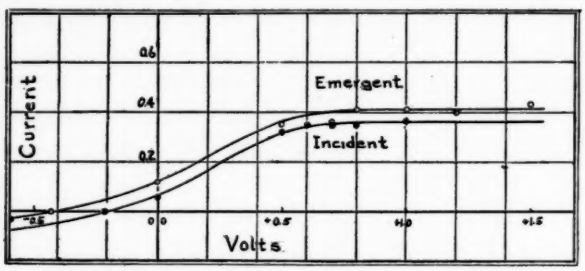

Fig. 3.

can be accounted for by the relative larger absorption of the film when facing away from the light than when turned towards the light.

The distribution of velocity curve for film 3 is given in Table II. The emergent and incident curves are too near alike to warrant a diagram to show the difference between the effects.

TABLE II.

Distribution of Velocity Curve for Film 3.

Difference of Potential in Volts.	Emergent Current. Divisions per Second.	Incident Current. Divisions per Second.
−2.0	−0.27	−0.16
−1.2	+2.5	+1.9
−1.0	4.8	4.0
− .8	6.4	6.3
− .6	15.0	12.0
− .4	19.4	20.0
− .32	25.0	19.0
− .2	30.0	25.4
∓ .0	38.0	33.7
+ .2	42.9	40.0
+ .32	45.4	44.1
+ .4	48.4	45.4
+ .6	50.0	48.0
+ .8	57.5	52.5
+1.0	65.9	57.5
+1.2	67.1	63.4
+1.6	71.8	69.5

$$\frac{E}{I} = \frac{1.884}{1.869} = 1.01$$

The number of electrons liberated are more than one hundred times as large as those from films 1 and 2. The saturation value of the current places this film just beyond the first maximum in the current-thickness curve.[1] Robinson showed that by plotting the ratio E/I for the maximum potential against E/I for the saturation current a film was found whose thickness was such that both ratios were equal to unity. The nearest experimental approach to this critical thickness are the values cited in the above table.

Fig. 4 represents the conditions for film 4 in Table I. The units of the current axis are ten times larger than those for curves Figs. 2 and 3.

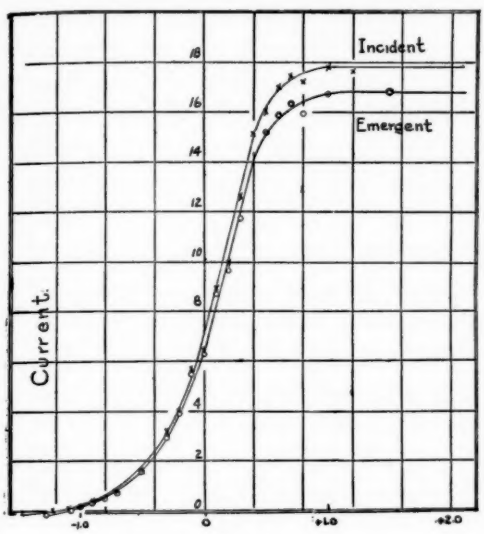

Fig. 4.

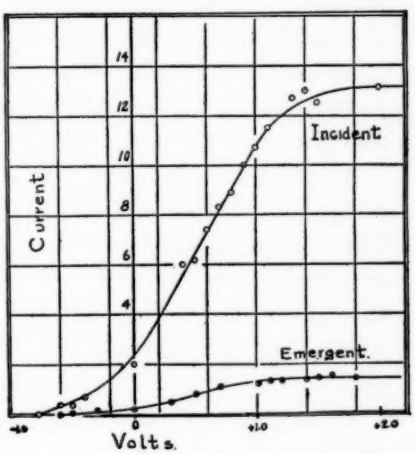

Fig. 5.

The incident velocities are now slightly larger than the emergent velocities. After this thickness the emergent velocities drop off faster than the incident, as seen in Fig. 5. This curve represents the conditions in a thick film. The emergent velocity curve is rapidly disappearing while the incident attains the normal value for platinum, equivalent to a film of infinite thickness.

DISCUSSION.

Evidently the most important results obtained are those from films whose thicknesses are less than 10^{-7} cm. Here both the ratios of emergent to incident velocity and current are greater than unity.

The current phenomena we have seen can partly be explained by Partzsch and Hallwachs' absorption curves, showing that the absorption for the emergent effect is greater than for incident effect, although the

[1] Loc. cit.

photo-electric current seems to be out of proportion to the absorption curves.

If the current effect were due to a layer of gas or double layer at the surface of the film, then this would effect thin films and thick films alike.[1]

Due to some secondary effect there may be a change in the coefficient of absorption of these thin films large enough to account for this sudden increase in current.

A view more in agreement with recent developments on the presence of "reactionsfähige gase" affecting the photo-electric current, would be the following. The relative difference between the observed photo-electric currents and the absorption curves as determined optically by Partzsch and Hallwachs, can be accounted for by the tremendous influence that various impurities in the residual gases, in which they were deposited, have on these films. S. Werner[2] has conclusively shown that platinum films deposited in various gases, although of equal thickness, possess very different photo-electric sensitiveness. They are also more sensitive than the metal itself.

At a thickness of 10^{-7} cm. the film may have special properties of occluding or absorbing the residual gases in which they are sputtered The photo-electric effect evidently depends upon these absorbed or occluded gases carried down with the particles of metal as they pass through the residual gases. For Hallwachs and Wiedman[3] have recently shown that the photo-electric effect of potassium could be obliterated by distilling the metal in vacuo, thus removing all intermolecular occluded or absorbed gases, while Kustner,[4] Fredenhagen[5] and Paech[6] have shown the importance of the presence of such gases to produce the well-known photo-electric effect of the various metals.

Since the photo-electric current is so largely influenced by the absorbed or occluded gases it might reasonably be concluded that the velocity of emission of the electrons is affected by these same conclusions. Because the above results show that a large increase in the photo-electric current is accompanied by a relative increase in the maximum velocity of emission.

Further experiments on other metals, using monochromatic light, are now under way. These we hope will throw more light on the diffi-

[1] O. Stuhlmann and K. T. Compton, loc. cit.

[2] S. Werner, Dissert. Uppsala, 1913; also Ark för Mat., Astron. Och. Fysik, 8, No. 27, S. 7, 1913.

[3] Wm. Hallwachs and G. Wiedmann, Ber. D. Phys. Ges., Jan., 1914, p. 107.

[4] H. Kustner, PHYS. Zs., XV (Jan.), p. 68, 1914.

[5] G. Paech., Ann. d. Phys., 43, p. 35, 1914.

[6] K. Fredenhagen, PHYS. Zs., XV (Jan.), 1914, p. 65.

culties underlying an explanation for the cause of the asymmetry in the velocities of emission.

I take great pleasure in acknowledging my indebtedness to Prof. A. W. Goodspeed, the director of the laboratory, for the generosity with which many special pieces of apparatus were purchased to complete this work.

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(To be continued.)

THE FACTORS WHICH DETERMINE THE QUANTITY OF ROENTGEN RADIATION GIVEN OFF BY AN X-RAY TUBE.

BY WHEELER P. DAVEY.

SINCE the discovery of Röntgen rays in 1895 there have been many methods proposed by which the quantity of this radiation might be measured. Physicians have almost without exception based their measurements upon the dehydrating, chemical, or photographic effects of the rays. If Röntgen rays are allowed to fall upon certain salts of the alkali metals, especially barium platino-cyanide, the crystals become dehydrated and their color is in consequence changed. The radiometers of Holzknecht (1902, 1910), Sabouraud-Noiré (1904), and Bordier (1906, 1910) are based upon this principle. They are subject to the criticism that the error of reading is great because the color change is small, that heat tends to discolor the crystals in the same manner as Röntgen rays, and that the very light which is used to detect the color change has a tendency to restore the original color. In 1903 Freund proposed a radiometer based upon the fact that Röntgen rays precipitated iodine from a mixture of iodoform and chloroform. The amount of iodine precipitated was determined by the color which it imparted to the liquid, but ordinary light was found to have the same action in discoloring the liquid as Röntgen rays. This method was improved in 1906 by Bordier and Galimard. In the same year Schwartz discovered that when a mixture of ammonium oxalate and bichloride of mercury was exposed to the action of the rays, a chemical reaction took place yielding calomel. He measured the amount of calomel precipitated by means of the amount of whitening it produced in the liquid.

In 1905 Kienböck brought out his "quantimeter" which consisted of strips of standardized photographic paper which were to be developed, after exposure to the rays, in a standard developer for a standard length of time at 18° C. By means of aluminum strips, an idea as to the penetrating ability of the rays could be gained at the same time. The quantity of Röntgen rays is determined by the amount of blackening of the paper. This method was perhaps an improvement in respect to the degree of accuracy obtainable. It is objectionable from the viewpoint

of the Röntgenologist in that the development of the paper must be made under very exact conditions, and that in cases where no more than a certain quantity of radiation must be used (as in therapeutic work), the rays must be cut off while a trial reading is taken. All six of the above schemes for measuring quantity of Röntgen rays have this objectionable feature,—the accurate matching of colors or tints is difficult, and in the case of some observers impossible.

Physicists have, in the main, confined themselves to two methods of measuring Röntgen rays. If the quantities to be dealt with were rather large, they have used the Kienböck papers. If the quantities to be measured were small, or if extreme accuracy were desired, they have resorted to the more delicate method of measuring the ionization produced by the rays. In the latter case it has been customary to employ either some sort of electroscope or an ionizing chamber connected to a quadrant electrometer. The chief experimental error in the ionization method has been due to "natural leak," *i. e.*, spontaneous ionization in the air. At certain seasons of the year, this source of error becomes so large that ionization measurements are almost impossible.

It would simplify the measurement for many purposes if the quantity of Röntgen rays could be measured in terms of the current through the tube, the potential difference across it, and the inverse square of the distance from the tube. The advantage of such a method would be that readings would be unaffected by climatic conditions, by the temperature or humidity of the room, by the kind or intensity of the illumination in the room, or by the sensitiveness of the observer's eye for small changes of tint or color. The accuracy of reading would be high. Further, readings could be taken while the tube is running, so that a definite quantity of rays could be obtained without the inconvenience and delay required by "trial readings." It would be impossible to compare, *in terms of voltmeter and millimeter readings*, results obtained on different outfits. This could be overcome by calibrating each outfit in terms of Kienböck or other units which can be measured by the direct action of the rays themselves. This result could then be reduced by means of the inverse square law to the quantity obtainable at a meter's distance.

In the early days such a method was proposed, but the current to be measured from a static machine or from induction coils of the size then in use, was very small, and the order of accuracy was therefore small. This coupled with the imperfections of the tubes of the time caused the method to fall into disuse. In 1904, Cardini[1] investigated this method of measurement and found, using a Holtz machine and a system of con-

[1] P. Cardini, N. Cimento, 7, pp. 241–259, Apr. 1904.

densers in series, that the quantity of Röntgen rays, as measured by ionization, was proportional to the energy expended between the terminals of the tube. In 1909, DeBeaujeu[1] reported a similar result, using currents not to exceed 1.5 M.A. Since the advent of modern high power generating outfits for X-ray work there has been considerable doubt as to whether Cardini's law is of universal application or whether it is merely a close approximation for a tube at small power input. The present work was undertaken to investigate this point, and, in addition, to find out whether the state of vacuum inside the tube was able to affect the quantity of Röntgen rays given off except in so far as it might help to determine the current at a given potential difference.

APPARATUS.

The generating plant consisted of a commutator transformer machine ("interrupterless machine") made by the Kny Scheerer Co. The secondary had a resistance of 113,000 ohms. The primary had a resistance of .265 ohm, and was operated on a 220-volt circuit. The E.M.F. of the secondary was controlled by inserting known resistances in the primary circuit by means of a rheostat. The commutator made use of 140° out of each 180° of the electric wave from the secondary of the transformer.

Two tubes were used, both of which had been pumped for use on a transformer by Green and Bauer. The first was a platinum target tube of standard type which had been in use for some time. It was in a nearly "stable" condition, softening a little on running and hardening after running. The other was a standard type of tube having a tungsten target and G & B cathode. It was in such a condition as to harden while running for all exposures made, except those above 20 M.A. In all cases, the tube hardened after running.

Current was measured by a moving coil milliammeter. Potential difference across the tube was measured by radiographs of a Benoist penetrometer[2] on Schleussner X-ray plates and reduced to readings on an electrostatic voltmeter, and to approximate readings on the equivalent spark gap between cones whose bases were 9 mm. in diameter and whose altitudes were 12 mm.

The quantity of X-rays was measured by the ionization in a zero-reading electroscope especially constructed so as to compensate in large measure for "natural leak." It consisted of a block of amber *A* sup-

[1] J. De Beaujeu, Ann. d' Electrobiol., Nov. 1909.

[2] The penetrating ability of an X-ray beam is expressed on the Benoist scale in terms of the thickness in millimeters of aluminium which offers the same opacity to the rays as is offered by a sheet of silver .11 mm. thick.

porting four squares of aluminum, B_1, B_2, B_3. B_4, B_1 and B_4 were permanently connected to a storage battery, giving a potential of 400 volts. D was a gold leaf which was permanently grounded throughout the experiment. A charge upon the gold leaf increased or decreased the sensitiveness of the instrument, depending upon the sign of that charge, so that if it had been desirable, the sensitiveness of the electroscope

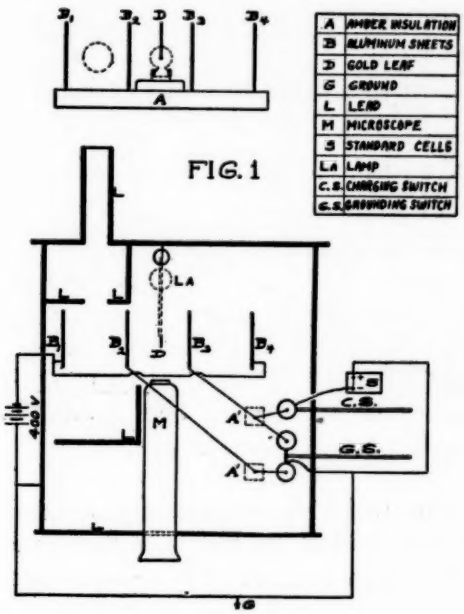

Fig. 1.

could have been altered by connecting D to some source of potential. The whole was completely screened from electrostatic influences and was behind a lead screen of sufficient thickness to cut out all the rays from the tube. The only radiations reaching the electroscope were the parallel rays entering as shown in Fig. 1 through a lead pipe, having a cylindrical hole $\frac{3}{8}$ inch in diameter. The distance from the target of the tube to the ionizing chamber was 19 inches.

Procedure.

The X-ray tube was brought into such a condition that, when run with 35.60 ohms in series with the primary of the transformer, the milliammeter showed a current of some predetermined amount. The rheostat was then adjusted so as to put whatever resistance was desired in series with the primary. Plates B_2 and B_3 were grounded and immediately insulated from each other and the ground. The tube was operated

for a predetermined interval of time. Plate B_3 was then charged by means of the standard cells until the gold leaf D came back to its original position. The amount of ionization produced by the rays was thus expressed in terms of the potential on B_3 necessary to cause a zero reading of the gold leaf. Any leak from B_1 to B_2 due to spontaneous ionization was almost entirely balanced by the corresponding leak from

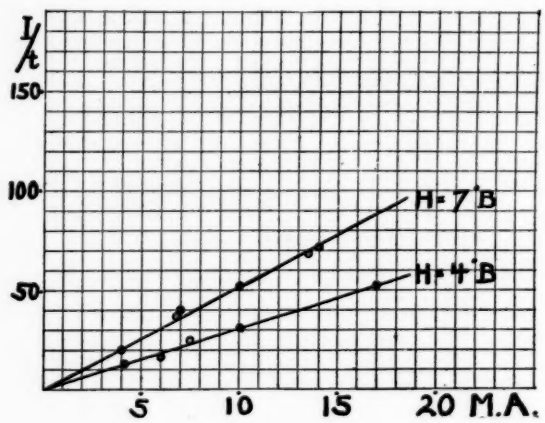

Fig. 2.

B_4 to B_3. Except for the few seconds after the tube was started in operation and before B_3 was charged, the leak from B_2 to D was almost entirely balanced by the leak from B_3 to D. The entire suppression of "natural

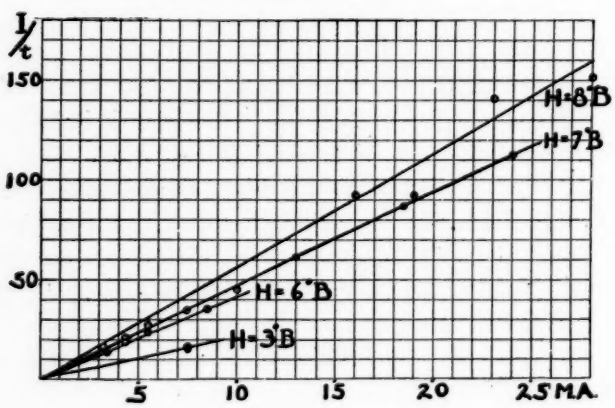

Fig. 3.

leak" is impossible, due to unavoidable slight asymmetry of the apparatus. But it was reduced to an amount so small as to be entirely negligible especially if the time of exposure to the rays is less than five

minutes. For exposures up to half an hour, the error due to natural leak was found to be so small as to be negligible for most purposes.

It was found that a potential difference of 300 V was necessary between B_1 and B_2, so as to insure saturation current from the strongest source of ionization used in the work. Care was therefore taken to so limit the time of exposure, that B_2 was never charged up to 100 V, thus leaving potential difference between B_1 and B_2 always in excess of 300 V. For this reason, the maximum current used through the tube was 28 M.A., as the time of exposure for larger currents was too short to make accurate readings on the milliammeter.

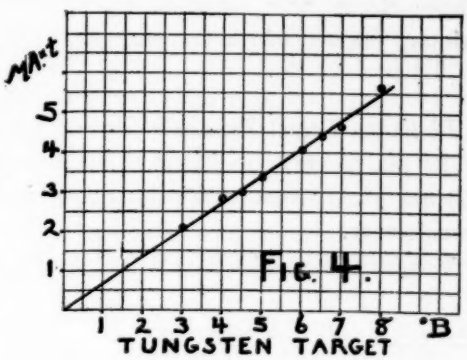

Fig. 4.

In the case of the platinum target tube, times were measured by means of an automatic time switch connected to the primary circuit of the transformer. This time switch gave only arbitrary time-units, and worked fairly well during the time of the experiment on the platinum

TABLE I.

Hardness in °B.	P.D. as Measured by Electrostatic Voltmeter.	Cm. Parallel Spark-Gap.	Condition of Tube.	Ohms Resistance in Series with Primary of Transformer.	Current in M.A.	Ionization.	Time in Arbitrary Units.	Ionization per Unit of Time.	Ionization per Unit of Time per M.A.	Average.	Ionization per Unit of Time per M.A. per °B.
4	25,000	6.6	B	35.60	4.1	90	7	12.8	3.1		
			B	29.10	6.0	85	5	17.0	2.8		
			B	23.70	7.5	85	3½	24.3	3.2		
			B	18.90	10.0	86	2¾	31.2	3.1		
			B	11.97	17.0	80	1½	53.3	3.1	3.1	.77
6	43,000	9.9	B	35.60	3.0	95	7	13.6	4.5		
			B	23.70	5.5	90	3½	25.7	4.7	4.6	.76
7	52,000	11.6	A	29.10	4.0	90	4½	20.0	5.0		
			A	18.90	6.8	92	2½	36.8	5.4		
			A	18.90	7.0	90	2¼	40.0	5.7		
			A	15.10	10.0	92	1¾	52.6	5.2		
			A	11.97	13.5	86	1¼	68.8	5.1		
			A	11.97	14.0	90	1¼	72.0	5.1	5.2	.74

Average ionization per unit of time per M.A. per ° B..... .76
Mean deviation from average..... 2 per cent.

target tube. But shortly afterwards, it became irregular in action, so that time on it was only accurate to 10 per cent. For this reason, when using the tungsten target tube, times were measured on a chronograph, whose circuit was operated by the same switch that controlled the primary current of the transformer.

RESULTS.

Platinum Target Tube.—Before each reading was taken, the tube was under one of two conditions of vacuum so as to take (*A*) 3.4 M.A. and (*B*) 4.2 M.A. when 35.60 ohms were in series with the primary of the transformer.

Tungsten Target Tube.—Before each reading was taken, the tube was

TABLE II.

Hardness in °B.	P.D. Across Tube Measured by E.S. Voltmeter.	Cm. Parallel Spark-Gap.	Condition of Tube.	Ohms Resistance in Series with Primary of Transformer.	Current in M.A.	Ionization.	Time in Seconds.	Ionization per Second.	Ionization per Second per M.A.	Average.	Ionization per Second per M.A. per °B.
3	16,000	5.0	E	23.70	7.5	80	4.90	16.3	2.1		
			E	23.70	7.5	80	5.00	16.0	2.1	2.1	.70
4	25,000	6.6	D	35.60	3.8	81	7.40	10.9	2.8	2.8	.70
4½	29,500	7.4	D	29.10	3.8	80	6.95	11.5	3.0	3.0	.67
5	34,000	8.3	D	29.10	4.5	85	5.45	15.5	3.4	3.4	.68
6	43,000	9.9	C	35.60	3.4	85	6.20	13.7	4.0		
			C	29.10	4.3	74	4.10	18.0	4.2		
			C	29.10	4.3	80	4.40	18.2	4.2		
			C	23.70	5.5	80	3.40	23.5	4.3		
			D	18.90	8.5	70	2.00	35.0	4.1		
			D	18.90	8.5	92	2.65	34.7	4.1	4.15	.68
7	52,000	11.6	C	35.60	3.2	75	4.90	15.3	4.8		
			C	29.10	4.3	71	3.40	20.8	4.8		
			C	29.10	4.3	71	3.50	20.3	4.7		
			C	23.70	5.5	85	3.10	27.4	4.9		
			C	18.90	7.5	85	2.45	34.7	4.6		
			C	15.10	10.0	90	2.00	45.0	4.5		
			C	11.97	13.0	92	1.50	61.3	4.7		
			D	9.40	18.5	87	1.00	87.0	4.7		
			D	9.40	19.0	72	.77	93.5	4.9		
			D	7.16	24.0	80	.71	112.6	4.7	4.7	.67
8	61,000	13.2	C	9.40	16.0	85	.90	93.4	5.8		
			C	7.16	23.0	96	.68	141.2	5.9		
			C	5.40	28.0	91	.60	151.6	5.4	5.7	.71

Average ionization per second per M.A. per °B..... .69
Mean deviation from average..... 2 per cent.

put under one of three conditions of vacuum, so as to take (*C*) 3.4 M.A., (*D*) 3.8 M.A., (*E*) 4.4 M.A. when 35.60 ohms were in series with the primary of the transformer.

The last column of both tables might equally as well have been expressed in terms of $\frac{\text{ionization}}{\text{time} \times \text{M.A.} \times \text{voltage}}$ or $\frac{\text{ionization}}{\text{time} \times \text{M.A.} \times \text{spark gap}}$ but the three are in direct proportion within the range used. In any case the quotients have no absolute value, as the measurements of ionization are only relative, the constant of the electroscope entering into all the results. An attempt was made to calibrate the electroscope by means of the γ-rays from a known quantity of radium, but was unsuccessful due to the difficulty of completely screening the plates *E* and *F* from the very penetrating γ-rays.

Summary and Conclusions.

1. An electroscope designed as shown above is practically free from the error due to natural leak when used under ordinary laboratory conditions. If occasion should warrant, it would seem possible to develop such an instrument for use under less favorable conditions than are usually found in laboratory practice.

2. With a constant potential difference across the terminals of the tube (*i. e.*, constant "hardness") the ionization per second (*i. e.*, the quantity of X-rays per second) is directly proportional to the first power of the current through the tube.

3. Except in so far as the state of vacuum in the tube helps to determine the current at a given voltage drop, it has no effect upon the quantity of radiation given off, at least within the ordinary working limits of a standard tube.

4. For rays from a given tube, operated by a given source of E.M.F., the quantity of radiation is directly proportional to the energy consumed in the tube. It is therefore only necessary for any given generating outfit to measure once for all by means of Kienböck paper, or other fairly reliable method, the quantity of Röntgen rays delivered at a meter's distance per kilovolt per milliampere per second. Thereafter all measurements of Röntgen-rays produced with that outfit may be made in terms of the energy (kilovolt-milliampere-seconds) per (meter),[2] sent through the tube, and translated in terms of Kienböck, Sabouraud or other accepted untis for purposes of comparison with data obtained on other outfits.

A part of the expense of this work was paid from a grant from the

Huntington fund to Prof. J. S. Shearer to further the work of standardization of Röntgen ray measurements for therapeutic purposes.

It is a pleasure to acknowledge my obligation to this source and to express my deepest thanks to Prof. E. L. Nichols and Prof. J. S. Shearer for their interest and hearty cooperation, and to my wife for her constant aid during the course of the work.

DEPARTMENT OF PHYSICS,
CORNELL UNIVERSITY.

THE MEAN DEPTH OF FORMATION OF X-RAYS IN A PLATINUM TARGET.

BY LAURA G. DAVEY.

W. R. HAM has shown[1] that X-rays are formed on an average, not on the surface of a target, but some little distance inside, this distance being called "the mean depth of formation" of X-rays. He was the first to measure this distance for any kind of target, using for his measurements a lead target.

The theory was as follows: If the normal to the target is not midway between the electroscopes (Fig. 1) the rays from a given point in the target have to pass through a greater thickness of the target in going to one electroscope than to the other. Let O (Fig. 1) be the source of an ether-pulse so situated as to be at the mean depth at which the X-rays originate. Let $l_1 - l_2 = x =$ the excess of target the pulse has to traverse in going to R over that which it traverses in going to L; $d =$ the distance from O to the point at which the cathode ray particle enters the target; $h =$ the perpendicular distance from O to the surface of the target; $\theta =$ the angle which the normal to the target makes with the cathode stream; $\theta_0 =$ the angle which the lines from the electroscopes to the target make with the cathode stream. Then

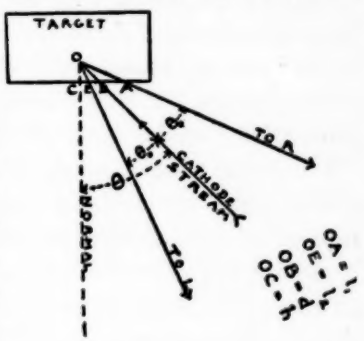

Fig. 1.

$$x = h\left\{\frac{1}{\cos(\theta + \theta_0)} - \frac{1}{\cos(\theta - \theta_0)}\right\}.$$

But

$$h = d\cos\theta.$$

Therefore

$$x = d\cos\theta\left\{\frac{1}{\cos(\theta + \theta_0)} - \frac{1}{\cos(\theta - \theta_0)}\right\}$$

or

$$x = d \cdot F(\theta, \theta_0).$$

[1] W. R. Ham, PHYS. REV., XXX., 1, Jan., 1910.

Let I_L = intensity of X-rays directed towards L,
I_R = intensity of X-rays directed towards R.
Then

$$I_R = I_L \epsilon^{-\lambda x}$$

where x is defined as above and λ is the coefficient of absorption found experimentally for the voltage used.

Ham has found that d for lead is 4.2×10^{-5} cm. at 14,000 volts and 6.4×10^{-5} cm. at 21,300 volts, thus proving that the mean depth of formation of X-rays is directly proportional to the potential difference across the tube. Ham's work was done with a specially constructed tube made from a bell-jar with windows of a uniform thickness inserted at the proper angles. The target was pivoted and was moved magnetically from the outside. The tube was attached to a Holtz pump during the entire time of taking readings so that there was always mercury vapor present. The means of excitation was a Holtz machine.

About a year later with the same apparatus W. P. Davey[1] measured the mean depth of formation in a silver target and found it to be 5.4×10^{-5} cm. at 10,000 volts and 9.2×10^{-5} cm. at 17,000 volts, thus confirming the fact that the mean depth of formation of X-rays is directly proportional to the potential difference across the tube.

It seemed that it would prove interesting to repeat the experiment with a standard platinum-target tube excited by a commercial "interrupterless" (transformer) machine. The thickness of the glass of various X-ray tubes was investigated and as long as the measurements were made on an arc whose plane was perpendicular to the axis of the tube the variations in thickness were negligible. This was to have been expected from the mechanics of glass blowing.

An attempt was first made to use ionizing chambers connected to a quadrant electrometer, thus using a null method much like the one of Ham, Lassalle and Smith[2] but this proved unsuccessful because of the disturbances due to the powerful variable static field of the transformer circuit. An arrangement was then set up as follows:

T (Fig. 2) is a platinum-target tube mounted so that it can be rotated through 180° about the axis OO. The target is set at an angle of 45° to the cathode stream.

SS and KK are thick lead screens.

CC are lead curtains over the apertures in KK which can be lowered to cut off direct radiation or raised to allow radiation to pass through.

BB are lead boxes serving to cut off secondary rays from the electro-

[1] W. P. Davey, Journal of the Franklin Inst., March, 1911.
[2] Ham, Lassalle and Smith, Jour. Franklin Inst., July, 1911.

scopes L and R, and (being permanently grounded) also acting as static shields.

L and R are set at an angle of 20° to the cathode stream. The amount of discharge of the electroscope is read by the microscopes MM.

The target was first turned so as to have its plane vertical and facing towards the electroscope L. Then the tube was brought into a definite condition (6° Benoist[1]) such that the electrostatic voltmeter V registered 43,000 volts. The electroscopes were charged to 200 volts. Then the tube was run approximately four seconds with the holes in KK closed by the curtains CC, thus giving the amount of discharge caused by spontaneous ionization and secondary radiation. Then the curtains were raised and the amount of discharge due to spontaneous ionization, secondary radiation, and primary radiation was observed. From these two readings the amount of primary radiation was computed. Then the tube was rotated 180° and readings were again taken both with curtains down and up. Lastly a piece of platinum .00269 cm. thick was inserted in the path of the rays going toward R and the above observations were repeated.

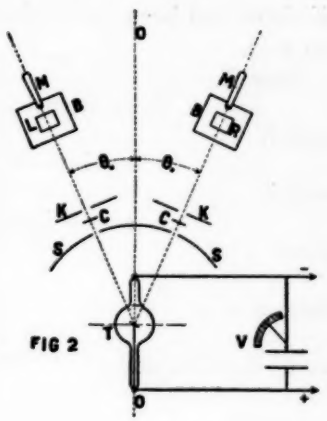

FIG 2

Fig. 2.

TABLE I.

TO FIND λ AT 6° B.

	R	L	R Corrected for Natural Leak and Secondary Radiation.	L Corrected for Natural Leak and Secondary Radiation.
Without Pt....	4.40	16.9	3.89	14.9
With Pt.....	1.51	16.0	1.00	14.0

In order to avoid inaccuracy due to inequalities in times of exposure the following method of treating the data was used. Without any platinum,

$$Lm = R,$$

where m is the factor of proportionality. From the above data,

$$m = \frac{389}{1490}.$$

[1] The penetrating ability of an X-ray beam is expressed in the Benoist scale in terms of the thickness in millimeters of Al which offers the same opacity to the rays as is offered by a sheet of Ag .11 mm. thick.

Therefore during the time the run was made with the platinum, R would have deflected

$$14m = \frac{339 \times 14}{1490} = 3.65$$

if there had been no platinum. But the platinum reduced the reading to 1.00.

Now if

I_0 = intensity of X-rays without Pt. = 3.65,

and if

I = intensity of X-rays with Pt. = 1.00,

and if

x = thickness of the Pt. = .00269 cm.,

then

$$I = I_0 \epsilon^{-x\lambda}$$

becomes

$$1.00 = 3.65\epsilon^{-.00269\lambda}$$

at 6° Benoist, and

$$\lambda = 481.$$

To Find the Mean Depth of Formation of X-Rays Inside the Platinum Target.

R was calibrated in terms of L as follows: If R and L were exposed to exactly the same radiation then the deflection of R might be expressed in terms of the deflection of L thus:

$$Rk = L.$$

Let R_1 = the reading of R when the target faces R,
L_1 = the corresponding reading of L,
R_2 = the reading of R when the target faces L,
L_2 = the corresponding reading of L.

Then,

$$\frac{R_1 k}{L_1} = \frac{L_2}{R_2 k},$$

from which

$$k = \sqrt{\frac{L_1 L_2}{R_1 R_2}}.$$

Table II.

	R	L	R Corrected for Natural Leak and Secondary Radiation.	L Corrected for Natural Leak and Secondary Radiation.
Target facing L...	4.05	20.1	3.79 = R_2	17.7 = L_2
Target facing R...	4.40	16.9	3.89 = R_1	14.9 = L_1

Whence

$$k = 4.23.$$

Therefore,

$$kR_1 = 4.23 \times 3.89 = 16.45$$

and

$$kR_2 = 4.23 \times 3.79 = 16.03.$$

We may therefore write,

TABLE III.

	I_L	$I_R = kR_2$	$I_R = kR_1$
When target faces L.....	17.7	16.03	
When target faces R.....	14.9		16.45

Now when the target faces L,

$$I_R = I_L\epsilon^{-\lambda x}$$

and when the target faces R,

$$I_L = I_R\epsilon^{-\lambda x}.$$

Hence,

$$\epsilon^{\lambda x} = \frac{17.7}{16.03} = \frac{16.45}{14.9} = 1.10$$

and

$$x = .00020- \text{ cm.},$$

$$d = \frac{x}{.891} = .00022 \text{ cm. at } 6° \text{ Benoist.}$$

Since it has been shown[1] that the depth of formation of X-rays in a target is directly proportional to the P.D. across the tube, and since this is directly proportional to the "hardness" of the tube in ° Benoist between the limits of 3° B. and 8° B., it follows that the depth of formation of X-rays in a platinum target in a tube of hardness H° B. is

$$\frac{H}{6} \times .00022 \text{ cm.} = .00004\, H \text{ cm. nearly.}$$

I wish to express my appreciation to Prof. E. L. Nichols and to Prof. J. S. Shearer for their many kindnesses throughout the course of the work and to my husband for aid in taking data.

DEPARTMENT OF PHYSICS,
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[1] W. R. Ham, loc. cit.; W. P. Davey, loc. cit.

A NEW DESIGN OF FLICKER PHOTOMETER FOR LABORATORY COLORED LIGHT PHOTOMETRY.

BY HERBERT E. IVES AND EDW. J. BRADY.

IT is now rather generally agreed that the difficulties of colored light photometry are best met in practice by eliminating the color differences through the medium of colored absorbing screens or auxiliary standards of different colors. Given the colored absorbing screens or other means the next matter is to determine their photometric transmissions or candle power values. In this determination all the difficulties of heterochromatic photometry must be faced, and a choice of instruments and photometric methods must be made. Later such choice must be made the subject of general agreement among the standardizing laboratories in whose hands such calibrating work should rest.

From a previous study of the subject[1] the conclusion has been drawn that the most desirable instrument for this purpose is the flicker photometer, but with the reservation that certain conditions of illumination and field-size must be adhered to and that the average results of many observers must be taken. Reference should be made to the original papers for the details of the work leading to these conclusions. The present paper describes a design of flicker photometer intended for the class of work mentioned and planned to be used in the manner specified.

Since a number of points of importance in the design of any flicker photometer were learned in the previous study, attention is here at the outset given to an account of these, as preliminary to the description of how these points have been provided for in the new instrument.

The attainment of high sensibility in a flicker photometer is dependent upon careful attention to several factors:

First, the dividing line between the two fields which are alternated should be a line without breadth,

Second, the speed of alternation should be accurately adjustable, and

Third, it should be possible to vary the relative brightness of the two fields quickly over a wide range with a minimum of physical effort.

The first point is quite as important in the flicker photometer as in the

[1] Philosophical Magazine, July, Sept., Nov., Dec., 1912, "Studies in the Photometry of Lights of Different Colors," Herbert E. Ives.

ordinary equality or contrast type. A thick dividing line in the latter instrument reduces the sensibility. In the flicker photometer a black line produces flicker of itself, necessitating a certain speed of alternation merely to make this mechanical imperfection disappear. As noted below, an unnecessary increase of speed decreases sensibility.

The question of speed in a flicker photometer is important, although the emphasis has often been laid on a mistaken idea. The speed determines the sensibility, and the speed necessary in any particular case is determined by the color difference. The speed does not affect the absolute values obtained, as has been thought by some, but it does change the accuracy of setting. For illustration, in Fig. 1 let AB be the photometer bar on which a flicker head is movable, having at A and B lights of equal candle power. If the speed of alternation is high enough (say, 70 or 80 alternations per second) the photometer head may be placed anywhere on the bar and no flicker can be perceived; this condition is represented by the line a–a. If the speed is now dropped to a certain lower value, it is found that at the ends of the bar flicker is visible, but for a long space in the center one point of setting is as good as another, (b–b). At each successive decrease of speed the region of uncertainty is decreased, hence the sensibility is increased. If the two lights are different in color this decrease of speed may be carried only so far as no perception of color alternation appears. The greater the color difference the higher must be the speed to prevent "color flicker."

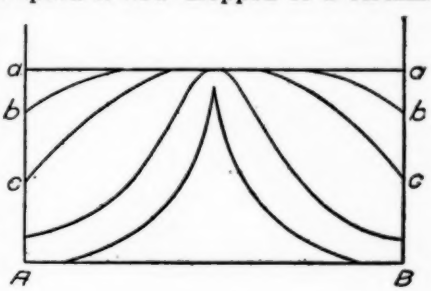

Fig. 1.

Graphical Representation of Speed-Sensibility Relations in the Flicker Photometer.

An interesting consequence follows from these considerations, namely, that with no color difference the speed demanded is zero, in other words, that the flicker photometer degenerates into an equality photometer in its limiting case where no color differences exist to call for the fusion due to alternation. Instructions which are sometimes given to the effect that the "correct" speed is to be determined with two lights of the same color and this speed then used with differently colored lights, are misleading, unless the speed called for by a bad dividing line is higher than that demanded by the color difference.

With regard to the third point, it is to be remembered that the position of match is that of minimum of flicker. Were the eye to maintain its

capacity to perceive flicker absolutely constant from moment to moment, to remain absolutely fixed in position, and were it possible to maintain the speed of alternation exactly the same, then the point of disappearance of flicker might be sought and worked up to slowly from each side. But in practice it is always best to adjust the speed until a very sharp minimum of flicker is produced. In finding a maximum or minimum point it is useless to approach from one side. Instead a series of oscillations about this point is necessary, the oscillations constantly decreasing in amplitude until the slightest touch either way increases the flicker. In order to produce these oscillations of brightness best, they should be producible by the easy motion of the hand or fingers. If a motion of the body is necessary, the eye also is apt to be moved from the photom-

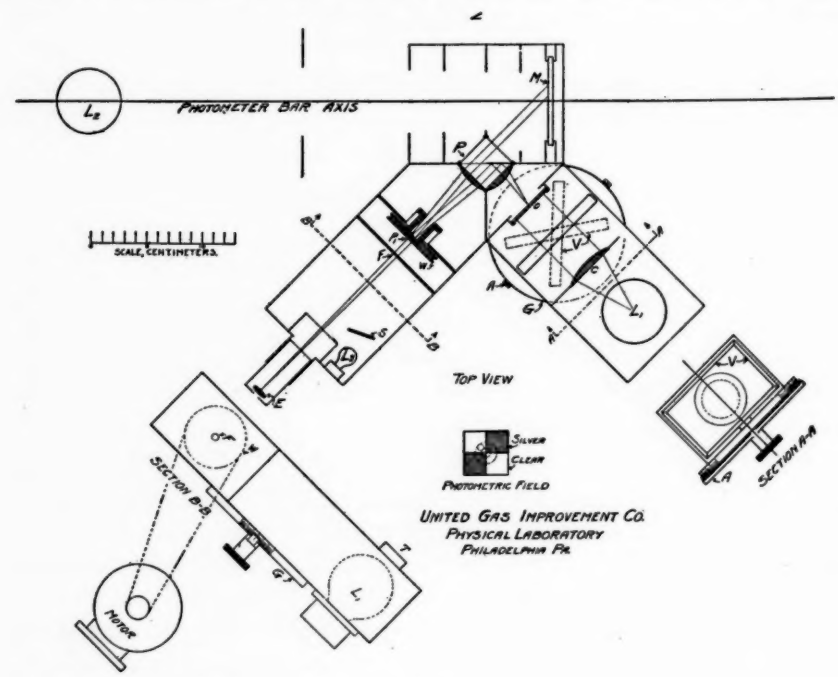

Fig. 2.

eter eye-piece and this movement, even when small, is seriously disturbing. It causes, beside the disturbance of attention, an increase of flicker just as a quickly moving object reveals the fluctuating character of an otherwise apparently steady light. Obviously a flicker photometer head should be of the stationary and not of the movable type.

The instrument is best described by reference to Fig. 2, which gives plan and sections. The photometer is planned to be used solely by the

substitution method, so that while the test and standard light sources are carried successively at appropriate places on the photometer bar, the comparison lamp is held at a fixed position in the photometer body. Tracing the paths of the beams of light which ultimately reach the eye will be the easiest way to understand the photometer's behavior. The light from the standard lamp (L_2) falls upon the matt white surface (M); thence a portion is reflected through the cube (P) and the small prism (P_1) to the eye. The light from the comparison lamp (L_1) passes through the lens (C); thence through the variable neutral-tint screen (V) to the flashed opal glass (O). Part of the diffused light of the latter enters the cube (P), is reflected through the small prism (P_1) to the eye-piece and eye at E.

The mechanism for producing the alternation of the two illuminations is comprised in the cube (P) and the prism (P_1). The cube is a modified Lummer-Brodhun. One of the component prisms is left untouched; the other is silvered and the silvering cut away in the manner shown in the separate sketch of the photometric field. In the present case the silver was cut away with a sand blast, after which the two prisms were cemented together with Canada Balsam, which practically eliminated the diffusing roughness of its surface originally caused by the sand-blast. The slight selective coloring, due to the silver, is of course of no importance, because of the substitution method employed. The small prism (P_1), having an angle of 10°, is mounted in a collar (W), which is rotated by the motor to which it is connected by a belt. The plate (F), perforated by a central round opening of 2° diameter, as viewed from the eye-piece, limits the actual area of the prism used. When the motor is running the beam of light which reaches the eye is, as it were, whirled around the axis of the instrument, alternating passing over the clear and the silvered parts of the cube (P). The successive appearance of the openings at F are readily seen from the separate sketch of the photometric field, where the small circle represents the section of the beam coming to the eye from F. The practically invisible dividing line between the silvered and the clear portion of the cube and the smooth continuous motion of the prism (P_1) insures the first condition considered above.

The second condition above dwelt upon is secured by using a series wound motor with a sliding variable resistance. In conjunction with the latter, sockets are provided in the base of the instrument for the insertion of various fixed resistances; these, together with the variable resistance, provide for any desired speed.

The third desirable condition is that in regard to easy variation of the relative illumination. This is here secured by the use of the variable

neutral tint screen (V). This consists of two opaque line gratings on glass slightly separated from each other. When rotated about an axis parallel to the lines the transmission[1] varies with a rapidity determined by the separation of the glasses. This screen is rotated by a milled head which also carries the pointer (A). The size of the milled head is such that it may be turned easily by the fingers. Small lights to illuminate the scale are also provided, but are not shown in the sketch, and the scale may be read either from the observer's side or else by an assistant viewing the other end of the pointer. The lens (C) is intended to help make the illumination on (O) uniform, and as a further refinement the cube (P) is furnished with a convex lens focused on one spot of the opal glass (O). A calibration curve of the screen in this particular

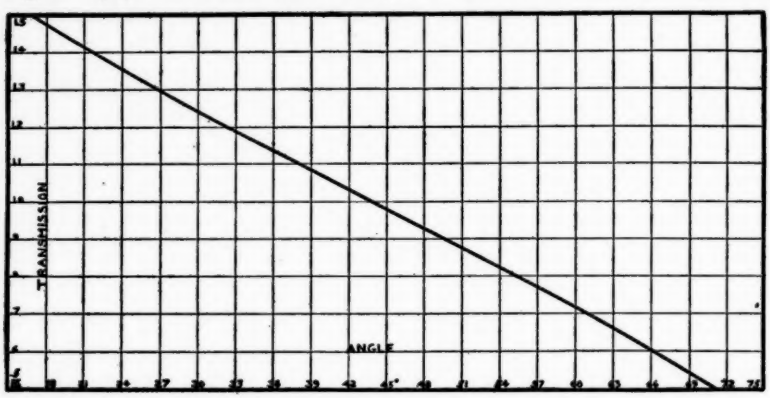

Fig. 3.

Calibration Curve of Variable Neutral Tint Screen.

instrument is shown in Fig. 3. It is practically a straight line over all the region which would be used, remembering that it is intended to have all measurements made at a single brightness (corresponding to 25 meter candles on a white surface), depending upon the variable screen merely for small ranges.

A novelty in this instrument is the means for illuminating the surroundings of the photometric field to nearly the same brightness, furnished by the small lamp (L_3) which throws its light on the white walls of the compartment facing F. S is a small translucent screen for securing uniform illumination. This bright surrounding field materially contributes to the comfort of reading.

Mechanical features of importance are the ventilating openings, of which one is illustrated at T, and the care taken to make every optical part immediately removable for cleaning. This latter is a point often neglected by instrument makers.

[1] "A Variable Neutral Tint Screen," H. E. Ives, Electrical World, Mar. 16, 1912.

The photometer in use thus far has proved itself admirably sensitive. A recent set of readings by two observers furnished the following figures, which are representative: With a very slight color difference between the comparison and test (incandescent electric) lamp the mean variation from the mean of ten settings by observer "A" was .38 per cent. and by observer "B" .45 per cent. With the test light a nearly monochromatic green (equivalent wave-length .546μ), the corresponding figures were .84 per cent. and .67 per cent. A set of seven readings on the same light source, the apparatus having been disturbed for other readings in between, showed an extreme variation from the mean of less than one per cent.

The instrument is now being used to calibrate certain absorbing solutions which have been developed to eliminate the color difference between the more important artificial illuminants and the ordinary carbon lamp standards.

PHYSICAL LABORATORY, THE UNITED GAS IMPROVEMENT COMPANY,
May, 1912.

A STUDY OF CONTACT POTENTIALS AND PHOTO-ELECTRIC PROPERTIES OF METALS IN VACUO: AND THE MUTUAL RELATION BETWEEN THESE PHENOMENA.

BY ALBERT E. HENNINGS.

THREE years ago Professor Millikan suggested as a promising subject for research, the careful study of the contact potential differences between metals in vacuo under conditions which would eliminate the effects of surface films. He considered it imperative that such a study be undertaken both because of the light which it ought to throw on the true nature of contact potentials and because his own photo-electric studies had produced evidence that the positive potentials acquired by metals under the influence of ultra-violet light were very probably related in some definite, but not yet fully understood way, to the contact potential differences between the metals. After carrying on preliminary experiments for a year or more with different types of tubes, the writer decided upon the experimental arrangement and designed the apparatus which have been used in the work herein reported.

The plan in brief was to test, simultaneously and in vacuo, the contact potentials and photo-electric properties of eight of the ordinary metals not only under conditions which have usually obtained in the study of either of these phenomena, viz., with surfaces prepared in air and subsequently surrounded by a vacuum, but also with surfaces mechanically prepared in a vacuum which was the best obtainable and which was maintained throughout all operations, and finally to observe the time changes in contact potential differences and photosensitiveness of photo-electrically or mechanically treated surfaces.

So far as I am aware no experiments have been made heretofore on the contact potential differences between metal surfaces freed from gas or oxide films. The chemical theory of contact potentials makes the whole effect depend essentially upon the existence of such films. Hence the significance of experiments of this kind upon the theory of contact potentials. Photo-electric experiments on clean surfaces in vacuo, however, have already been made and described by Pohl and Pringsheim,[1]

[1] Verh. d. Deutch Phys. Ges., 13, 474, 1911; 14, 46, 506, 546, 1912.

and Hughes,[1] using freshly distilled surfaces and by Herrmann,[2] Richardson and Compton,[3] and Page,[4] using mechanically cleaned surfaces.

THE RESULTS.

The facts which may be considered as having been definitely established by the present investigation are the following:

1. The contact potentials of the metals are not noticeably changed by differences in pressure ranging from atmospheric pressure to that of the best vacuum obtained.

2. All the metals are rendered more electro-positive when polished in vacuo and gradually become more electro-negative just as do freshly polished surfaces in air.

3. Prolonged illumination with ultra-violet light greatly modifies the contact potentials of film coated surfaces, and whatever the direction or magnitude of the change may be each metal exhibits a tendency to recover its original potential when the action of the light has ceased. With newly prepared surfaces these changes are negligible or inappreciable.

4. On the photo-electric side the results as a whole confirm the point of view adopted by Richardson and Compton in regard to the relation between photo- and contact potentials.

5. The photo-sensitiveness of all the metals is very largely increased when the surface films, which in general always exist even in the best vacuum unless the metals have been subjected to special treatment as described below, are removed.

6. Although the order of the metals when arranged according to their photosensitiveness in vacuo is usually not at all that of the Volta contact series, the order assumed by freshly cleaned metals approaches very closely that of this series.

DESCRIPTION OF APPARATUS AND OUTLINE OF EXPERIMENTAL PROCEDURE.

The apparatus designed for this study is enclosed in a glass bulb about 13 cm. in diameter with five projecting arms—four being in the horizontal plane and the fifth occupying a vertical position—the axes of all meeting at the center of the bulb. Fig. 1 represents a horizontal section in the plane of the intersecting axes of the two pairs of projecting arms and Fig. 2 represents a vertical section in the plane including the vertical

[1] Roy. Soc., Phil. Trans., 212, pp. 205–226.
[2] Verh. d. Deutch Phys. Ges., 14, 557, 1912.
[3] Phil. Mag., 24, pp. 575–594.
[4] Amer. Jour. Sci., 36, 501, 1913.

axis and that of one of the pairs of projecting arms. The horizontal arms are 42 to 45 mm. in diameter.

Eight metals, magnesium, aluminum, zinc, tin, iron, brass, copper, silver, in the form of disks 2 cm. in diameter are mounted upon an amber

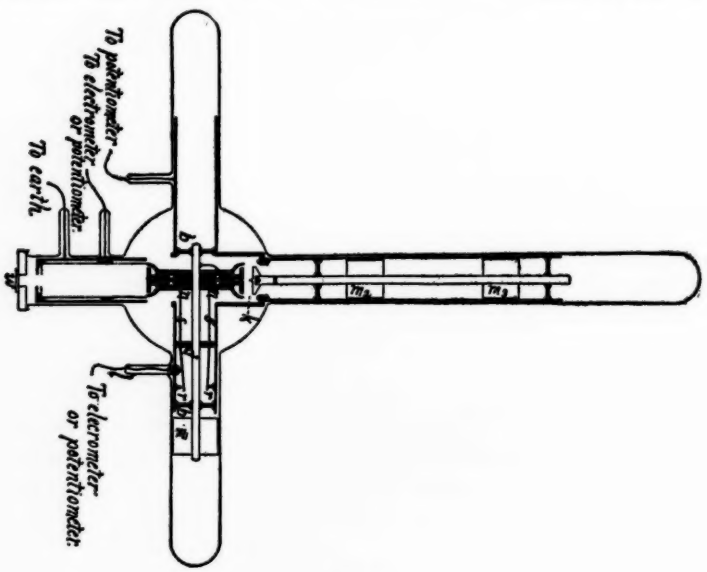

Fig. 1.

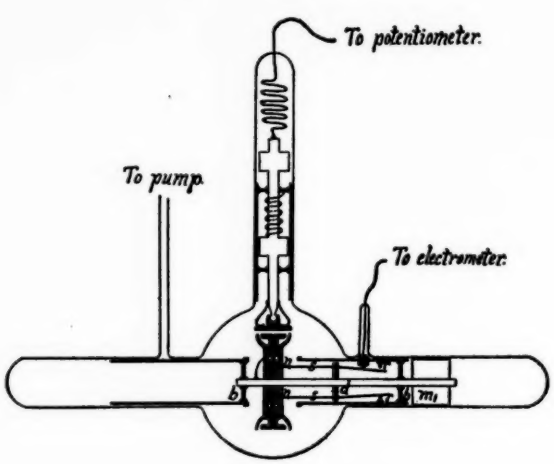

Fig. 2.

hub 38 mm. in diameter with the planes of their faces parallel to the axis of the wheel so formed. To one end of the rod passing through the hub and supporting it by means of suitable bearings *b*, *b*, in brass tubes

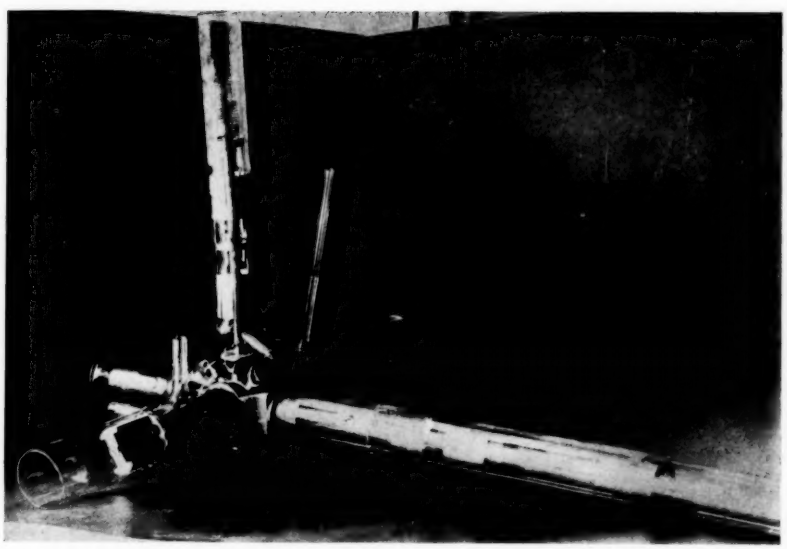

Fig. 2*a*.

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joined rigidly together and fitted firmly in the projecting arms of the bulb is attached a double anchor-shaped piece of iron, m_1. By means of an external electro-magnet the wheel may be rotated and if necessary moved a short distance along the axis, making it possible to adjust very accurately the position of any of the eight metal disks.

The longest of the projecting arms is fitted with a brass tube which is attached to, and holds rigidly together, the brass tubes which support the axle of the wheel. This tube serves also to give support to the bearings for a rod carrying at its inner end a well-tempered wedge-shaped steel tool, k, 2 cm. wide, and at two other points the iron armatures, m_2 and m_3. The latter by means of a second external electro-magnet may be rotated and moved along the axis. The knife-edge is thus made to rotate and simultaneously to press against the surface of one of the metal disks brought into juxtaposition. By this device all of the eight metal surfaces were effectively scraped off in vacuo. With the softer metals precaution had to be taken so as not to cut away too much. To insure the successful operation of this device the knife carries at its middle point a thin conical projection which fits into a hole in the center of the disk. In order that the knife may always bear upon the whole surface the rod is jointed very near its inner end.

The shortest of the projecting arms carries a brass cylinder with an inner concentric one of a double layer of fine meshed wire gauze. Both cylinders were blackened by oxidation and are insulated from each other with amber. The further end of the double cylinder so formed is closed save for a central circular opening 11 mm. in diameter through which ultra-violet light may be directed upon one of the metal disks when brought into such a position as to practically close the double cylinder at the inner end which is open and as near the wheel as possible without interfering with its motion. The ultra-violet light is admitted through the thin quartz window, w, which closes a circular opening 9 mm. in diameter in a heavy glass plate. Both the quartz and glass plates are sealed on with de Khotinsky cement. The outer brass cylinder was earthed in this work and the inner one of gauze was used as the receiving electrode for the measurements of the photo-currents.

The metal under investigation is insulated from all the rest by means of the commutator arrangement now to be described. Leading from the brass nuts, n, into which the rods attached to the metal disks are screwed, are the heavy steel wires, s, one for each of the disks. These wires are held apart by the amber disk, d, which is fixed upon the axle of the wheel, and which causes the wires to press against an immovable ring, r, inserted inside the brass supporting tube. When the wheel

rotates each wire slides over and remains in contact with the inner surface of this ring except at two points in a complete revolution, one when the disk to which the wire is attached is in position for ultra-violet light illumination and the other when it is in position for the measurement of the contact potential. (This latter position will be indicated and the manner in which the measurement is made will be described presently.) At these two points the steel wire is forced to break contact with the ring by means of a curved piece of brass which is insulated by means of amber. The platinum wire, *l*, leading to the brass is then in communication with the now insulated disk. To insure the best possible contact the curved piece of brass and the brass ring are faced with platinum and each of the wires at the two points where contact is made is likewise covered with platinum. There is a second amber disk (omitted from the diagram to avoid confusion) placed near the end of the wires, which is slotted radially and which serves to prevent each wire from being carried around by the friction between it and the surface with which it is making contact. The plate under illumination may be charged to various potentials and the distribution of velocity curve determined by observing the rate with which the wire gauze cylinder used as receiving electrode charges up. This procedure was the one adopted for the major portion of the photo-electric data recorded in this paper. Measurements of the positive potentials acquired by the insulated plate when exposed to ultra-violet light were also made by putting the plate in communication with the electrometer and applying the accelerating or retarding potentials to the wire gauze cylinder.

The vertical arm supports by means of an inserted brass frame a spool-shaped piece of iron which carries at its lower extremity a brass plate $3\frac{1}{2}$ cm. in diameter. A solenoid outside the tube is used to raise or to lower the brass plate, which with each of the metal surfaces in turn constitutes the condenser system employed in determining the contact potentials. The metal disk which is to be examined when brought into position directly beneath the vertical tube is insulated by the commutator device already described. The two surfaces are brought near together by lowering the brass plate upon the three projecting arms which surround, but are insulated from, the disk. The plane of the points of these three arms was made as nearly parallel as possible to that of the disk and about .12 mm. (before the surfaces were scraped) above it. It is not essential that the two planes be absolutely parallel if for each combination the relative position of each of the surfaces when near together is always exactly the same. The brass plate must therefore never fail to rest upon all three points when lowered. This condition

is met by having the brass plate upon a ball and socket joint. Between the rod above the joint and the back of the plate are attached also three brass springs, the purpose of which is to make certain that the movable plate is kept horizontal when it is being moved away from the disk beneath. A portion of the weight of the iron spool is born by a spiral spring attached between it and the supporting frame in order that the solenoid need not be inconveniently large.

Theoretically the simplest way to determine the contact potential between the brass plate and the metal disk underneath would be to place such a potential upon the brass plate and all the metal parts of the apparatus except the metal disk under observation which is in communication with the electrometer and which is first grounded and then insulated, that no deflection of the electrometer needle is observed upon raising the brass plate, but practically this procedure is not sufficiently expeditious. It proved far more satisfactory to apply to the movable plate and the framework some convenient positive potential and then with a reversing key, the same negative potential, observing in each case the electrometer deflection when the upper plate was raised. Proceeding in this manner the contact potential difference is determined by the relationship

$$E = PD\,\frac{d_1 + d_2}{d_1 - d_2},$$

where

E represents the contact potential difference.

PD represents the potential positively or negatively applied to movable plate.

d_1 represents deflection when $+ PD$ is applied.

d_2 represents deflection when $- PD$ is applied.

The deflections must of course be taken with their sign. The mean of these two deflections is the deflection observed with no charge applied to the movable plate. The several metals are thus compared with the brass plate. The contact potential difference between any pair may be taken as the difference between the contact potential differences of each of the pair with brass.

Preliminary Measurements of the Contact Potentials.

When the parts of the apparatus had been assembled in the bulb, the contact potentials were measured before sealing up the tubes through which the various parts had been introduced. The numbers in the first column in Table I. represent the values in volts observed for each of the metals when compared with the movable brass plate. The second

column gives a series of values obtained with the closed tube after remaining for several days filled with ordinary air at atmospheric pressure. The third column gives the value for dry air, *i. e.*, the air had been pumped out and dry air introduced, the process being repeated a number of times and the apparatus then left to stand several days after sealing up with drying tubes of phosphorus pentoxide. The bulb was then again exhausted and left so for three days, when it was again filled and exhausted. The results given in columns III., IV., V. and VI. exhibit nothing which can be attributed to changes in pressure. The seventh column gives the values obtained with a very low vacuum which had been reached after several days pumping with a Töpler pump and the use of cocoanut charcoal. The remaining columns give the values obtained in succeeding intervals during all of which time the best possible vacuum was maintained. Mercury vapor was prevented from entering the bulb by means of gold foil which filled the glass tube leading to the pump for 40 cm. of its length.

TABLE I.

Metal.	I. Mar. 17, Open Tube Atmos. Pressure.	II. Apr. 25, Sealed Tube Atmos. Pressure.	III. May 16, Atmos. Pressure.	IV. May 18, Vacuum.	V. May 19, Vacuum.	VI. May 20, Atmos. Pressure.	VII. June 3, Vacuum.	VIII. July 1, Vacuum.	IX. July 17, Vacuum.	X. July 24, Vacuum.
Silver	−.16	−.11	−.076	−.076	−.080	−.081	−.073	−.081	−.079	−.084
Tin	+.29	+.31	+.296	+.291	+.285	+.281	+.260	+.248	+.230	+.232
Magnesium	+.98	+.95	+.918	+.911	+.904	+.894	+.890	+.87	+.88	+.86
Zinc	+.35	+.32	+.300	+.295	+.296	+.289	+.285	+.267	+.254	+.248
Aluminum	+.50	+.45	+.428	+.419	+.417	+.410	+.422	+.394	+ 382	+.373
Iron	−.017	+.02	+.031	+.031	+.026	+.027	+.030	+.027	+.038	+.030
Copper	−.08	−.06	−.054	−.062	−.048	−.057	−.059	−.067	−.067	−.075
Brass	−.03	−.02	−.017	−.015	−.022	−.026	−.028	−.034	−.032	−.032

A survey of all the results in Table I. shows that the contact potentials must be independent of pressure. None of the changes are abrupt, indicating that they are all due to the mere ageing with time. The metals on the whole have become more electro-negative. This does not appear to be true in all cases, but the apparent discrepancy lies in the fact that the brass plate with which these metals have been compared is also subject to changes.

THE EFFECT OF ILLUMINATION WITH ULTRA-VIOLET LIGHT UPON THE CONTACT POTENTIALS OF FILM COATED SURFACES.

The illumination of the surfaces of the metals with ultra-violet light was effected through the quartz window from the mercury-in-quartz

arc which was fed by a current of 1.85 amperes. The arc was placed about 20 cm. from the disk to be illuminated. By means of diaphragms with circular openings of various sizes it was arranged that the *whole* surface of the disk was acted upon by the light. (It is essential that the whole surface be illuminated, for if the light modifies the surface, the face of the disk remains no longer homogeneous. It is not possible to determine the exact change effected in the contact potential by the

TABLE II.

Metal.	Contact P.D.'s Before Illumination.	Contact P.D.'s After Illumination for 10 Min.	2 Hrs. Later.	6 Hrs.	20 Hrs.	30 Hrs.	42 Hrs.
Silver	−.087	−.082	−.078	−.084	−.084	−.087	−.085
Tin	+.225	+.326	+.318	+.306	+.263	+.240	+.229
Magnesium	+.87	+.79	+.84	+.85	+.87	+.85	+.86
Zinc	+.244	+.352	+.347	+.325	+.288	+.252	+.238
Aluminum	+.367	+.333	+.350	+.355	+.362	+.373	+.370
Iron	+.033	+.075	+.072	+.067	+.064	+.056	+.053
Copper	−.070	−.166	−.125	−.117	−.097	−.096	−.096
Brass	−.034	−.137	−.083	−.070	−.047	−.044	−.041

light unless it be known just what fraction of the surface was illuminated. The contact potential of such a composite surface would be the average of the modified and unmodified portions of the surface.) Tables II. and III. show not only the manner in which contact potentials of film-

TABLE III.

Metal.	Contact P.D.'s Before Illumination.	Contact P.D.'s After Illumination for 2 Hours.	4 Hrs. later.	10 Hrs.	1 Day.	2 Days.	3 Days.	8 Days.
Silver	−.086	−.076	−.077	−.080	−.077	−.083	−.080	−.095
Tin	+.225	+.357	+.345	+.276	+.263	+.244	+.242	+.254
Magnesium	+.87	+.57	+.67	+.74	+.79	+.81	+.83	+.848
Zinc	+.264	+.540	+.452	+.362	+.293	+.287	+.287	+.237
Aluminum	+.362	+.193	+.286	+.333	+.346	+.353	+.343	+.372
Iron	+.042	+.093	+.090	+.087	+.084	+.080	+.087	+.082
Copper	−.083	−.195	−.142	−.113	−.105	−.096	−.095	−.100
Brass	−.045	−.190	−.111	−.088	−.080	−.063	−.072	−.072

coated surfaces are modified under the influence of ultra-violet light but also the manner in which the metals recover from the effect.

Several similar series of measurements were made and in all cases magnesium, aluminum, copper, and brass became more electro-negative,

while silver, tin, zinc, and iron became more electro-positive under the action of the light. With prolonged illumination the changes brought about in the contact potentials are greater and the recovery of the metals is in general less rapid and less complete than when the surfaces are exposed for but a short time, for it is seen that with ten minutes' exposure, Table II., to ultra-violet light, the recovery is on the whole more complete than with two hours' exposure, Table III., indicating that in the latter case the surfaces have been more or less permanently modified. By using much intenser illumination than that used in these cases, it was possible to produce even greater changes. Thus, zinc and magnesium, the one becoming more electro-positive and the other more electro-negative, could be made to change their order in the contact potential series.

There is no doubt that film coated surfaces are modified by ultra-violet light, but the fact that both positive and negative effects may be produced finds no ready explanation. If all the surfaces had become more electro-positive it might be supposed that they had been to a certain extent freed from gas or oxide films. On the other hand if all had become more electro-negative, it might be supposed either that a film or some modification equivalent to one had formed or that electrons freed from the metal had imbedded themselves in a film already existing. It is probable that something of the nature of both of these possibilities exists and what is observed is a resultant effect which depends upon the individual characteristics of the film and the metal. In any case it is almost certain that the surface becomes a non-homogeneous one, if not indeed already such, so that the measurements give merely the average effect of the constituents of the composite surface.

THE RELATION BETWEEN CONTACT AND PHOTO-POTENTIALS WITH FILM-COATED SURFACES.

Compton has shown[1] that the contact potentials of photo-electrically excited metals must be considered in conjunction with the applied accelerating potentials in measurements on photo-currents. By using different receiving electrodes he found that the distribution of velocity curves were all of practically the same shape but merely separated with reference to each other along the voltage axis by amounts equal to the contact differences of potential between the electrodes. Richardson and Compton[2] using analyzed light, found that for all wave-lengths and for all the metals, the maximum currents were reached when the potential

[1] Phil. Mag., 23, pp. 579–593, Apr., 1912.
[2] Phil. Mag., 24, pp. 575–594.

difference between the excited plate and the receiving electrode was zero volts, proper account of course being taken of the contact potential differences. These contact potential differences were not measured under the conditions which obtained when the metals were under examination but were assumed to be the same as those for undisturbed surfaces in air. This assumption may not always be correct, although it seems to have been so in their experiments. Their point of view, however, in regard to the manner in which contact potential differences are to be taken into account is supported by this work.

TABLE IV.

Metal.	Contact P.D.'s Against Brass Plate.	Accelerating P.D.'s for ¾ Saturation.	Contact P.D.'s with Copper.	Differences in Accelerating P.D.'s.
Silver	−.08	−.25	+.11	+.07
Magnesium	+.53	−.89	+.72	+.71
Zinc	+.49	−.91	+.68	+.73
Aluminum	+.23	−.53	+.42	+.35
Tin	+.28	−.69	+.47	+.51
Iron	+.09	−.45	+.28	+.27
Brass	−.18	−.16	+.01	−.02
Copper	−.19	−.18	00	00

Owing to the fact that film coated surfaces suffer changes when excited, it was difficult to duplicate distribution of velocity curves or to determine accurately the point at which the saturation current is reached. Therefore, instead of plotting the complete curve or locating the point at which saturation occurs, merely the saturation current was found and then such a potential was applied to the excited plate that the current was reduced to three fourths of the saturation value. This was indeed an arbitrary proceeding but nevertheless one giving reliable and definite information in regard to the general way in which the contact potentials and accelerating potentials are related. Table IV. gives a sample series of results obtained when the plates had been previously strongly illuminated in order to bring them into a modified condition which could be approximately maintained. The last two columns indicate a fair agreement between the differences in the contact potential differences and those in the accelerating potentials. Exact agreement is not to be expected for the applied potential necessary to produce the saturation current from a given metal is a variable quantity depending on the condition of the surface. In fact the complete velocity curve may be greatly altered in its general shape and inclination as well as shifted bodily along the voltage axis by changes in the surface.

The apparent initial velocities of emission of the electrons from illuminated surfaces are thus also dependent upon surface conditions. Nor is this dependence such as always to make the modifications in the contact potentials responsible for some of the changes observed to take place. Thus in the case of magnesium, which was found to become more electro-negative with illumination, the initial velocities of emission became greater just as though the surface had become more electro-positive rather than more electro-negative. In seeking an explanation of this fact, it may be supposed that the film covering the surface is, if not neutral, neither strongly positive nor negative, and in parts at least not of sufficient thickness to screen off the intrinsic contact effects of the metal itself. Then it is possible also to conceive of this film as being broken up by illumination in such a way as either to present more relatively inactive surface or to increase its screening effect while at the same time the broken film allows the electrons to escape more readily than before. Such an explanation is strengthened by the additional fact that the magnesium surface after a considerable period of rest, thus permitting the formation of a film, would become increasingly photo-sensitive with a somewhat prolonged exposure to ultra-violet light.

CONTACT POTENTIALS WITH NEWLY PREPARED SURFACES IN VACUO.

The only way to prepare a pure and approximately film-free surface of any of the ordinary metals is to cut away the metal. If this is done in a good vacuum, the best possible conditions have been established for the study of the properties of clean metallic surfaces. It was for this reason that provision was made to scrape off the old surfaces in

TABLE V.

Metal.	Contact P.D's Before Scraping.	Contact P.D's After Scraping.	24 Hrs. Later.	2 Days.	4 Days.
Aluminum.....	+.293	+1.04	+.94	+.895	+.874
Iron.....	+.053	+ .24	+.217	+.205	+.192
Copper.....	−.106	+ .10	+.060	−.068	−.110
Silver.....	−.097	+ .05	+.021	−.003	.000
Tin.....	+.216	+ .32	+.330	+.324	+.317
Magnesium.....	+.825	+1.47	+.81	+.724	+.713
Zinc.....	+.193	+ .64	+.56	+.512	+.496
Brass.....	−.123	+ .26	+.243	+.227	+.228

vacuo. As soon after the scraping was done as adjustments could be conveniently made, the contact potentials against the movable brass plate were measured. The best obtainable vacuum was maintained

throughout. In Table V. the first column gives the values observed just before, and the second column those just after, polishing. The metals are all more electro-positive as a result of polishing, just as would have been the case had the operations taken place in air. As the last three columns show, the metals tend to become more electro-negative with time, the rate of change being relatively quite different for the different metals. It is interesting to note that after four days copper and magnesium have become more electro-negative than they had been at any time previous to the scraping except when recently subjected to the action of the ultra-violet light.

TABLE VI.

Metal.	Contact P.D.'s Before Illumination.	Contact P.D.'s After Illumination.
Silver	+.010	+.014
Magnesium	+.753	+.760
Zinc	+.513	+.498
Aluminum	+.953	+.961
Tin	+.305	+.312
Iron	+.189	+.200
Brass	+.222	+.215
Copper	−.068	−.077

Agreement has not yet been reached in regard to a theory of the true nature of the phenomenon. These results, however, do not strengthen an electrolytic theory, but tend rather to support the view that the pure metals exhibit definite and characteristic potentials because of intrinsic properties which manifest themselves in this manner at the surface. Chemical action is to be considered not so much because of itself as because of the products resulting from it. When a metallic surface has become oxidized or is covered with any sort of a film, the effect observed is essentially that of a composite surface, both film and metal contributing to the general effect except when the film is of such thickness or so disposed as to screen off entirely the effects of the metal.

This point of view is further supported by the fact that with clean surfaces in vacuo, exposure to ultra-violet light produces a little or no change in the contact potentials. Table VI. gives the values obtained before and after 15 minutes' illumination with surfaces which had been prepared about 24 hours previously. It was decided to examine them at this stage in order that the ageing effect which proceeds more rapidly shortly after the scraping of the surface has taken place than it does later, would not mask such changes as might be produced by the action of the light. The changes observed are not great enough to make it

possible to assert positively that they are brought about by the illumination. Even if they are due wholly to the action of the light, they are so small relatively that, for the short intervals of illumination which usually obtain in photo-electric studies, it may be safely assumed that no appreciable changes in the contact potentials of surfaces recently prepared in vacuo take place as a result of exposure to the light. It is certain, however, that even with surfaces prepared in vacuo, the presence of films is not completely eliminated. They must begin to form as soon as polishing ceases but it may be taken for granted that they are very much thinner and cover more imperfectly the metals underneath than the old films which were removed. The metals are therefore exposed more directly to the light and hence the results in Table VI. show that the metals themselves are not modified so far as their contact potentials are concerned. On the other hand, since with old films great differences are produced it is more than probable that all the changes which are observed in contact potentials as a result of photo-electric treatment are due to modifications brought about in these films.

PHOTO-CURRENTS FROM SURFACES RECENTLY PREPARED IN VACUO.

The distribution of velocity curves with surfaces recently prepared in vacuo were plotted and are shown in Figs. 3 to 8. They are arranged in pairs and some are repeated in order to show more clearly the relations

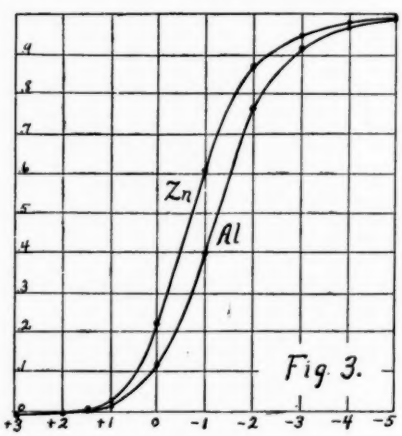


Fig. 3.

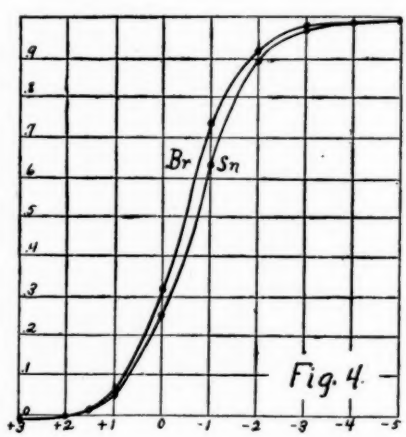


Fig. 4.

existing between them. All have not been shown in a single figure in order to avoid confusion. When −8 volts were applied to the illuminated disk, the photo-current was approximately a maximum in all cases. In plotting the curves this current is taken as unity. There is a slight

effect due to reflected light as indicated by the fact that the velocity curves cross the axis of zero current. This makes it impossible to determine the true positive potentials acquired by the metals when illuminated with unanalyzed ultra-violet light. It is interesting to note, however, that except in the case of magnesium, the point at which the axis is crossed by these curves is approximately the same for all the metals, lying between +1.7 and +1.9 volts. The true positive potential is undoubtedly somewhat greater and it would seem that with perfectly clean surfaces it is the same for all the metals. If this is the actual state of affairs, the more electro-positive a metal is, the greater is the retarding potential, taking into account of course the contact potential of the metal,

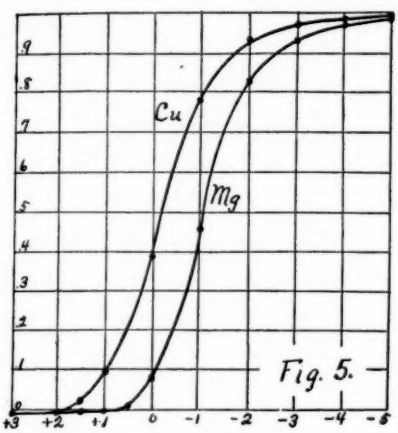


Fig. 5.

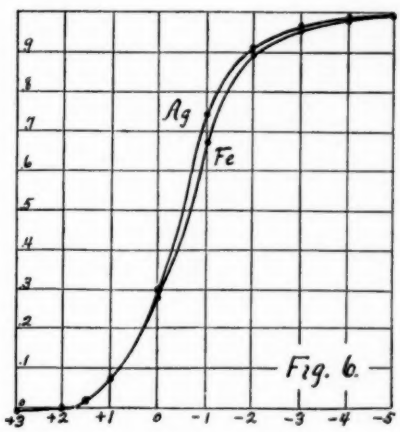


Fig. 6.

necessary to keep the electrons from escaping. For magnesium this point, in the case of the curve plotted, corresponds to about +.7 volt. This does not mean that magnesium differs fundamentally from the other metals. It must be mentioned that these curves were not plotted until a few hours after scraping for the reason that the photo-sensitiveness of newly formed surfaces decreases very rapidly with time. This is particularly true of magnesium. It was necessary, therefore, that the surface be old enough that its photo-sensitiveness remain practically unchanged during the interval necessary to make the observations for a complete curve. Consequently the surfaces cannot be considered absolutely free from films, for these are sure to form even in the best obtainable vacuum. The magnesium surface, as would be expected from the readiness with which it oxidizes, merely shows in a more striking manner any modification that may be taking place. With magnesium surfaces newer than the one for which the curves are shown, the current

axis is crossed at points farther to the left, *i. e.*, the more or less common point for the other metals is approached nearer and nearer the newer the magnesium surface. With older surfaces this point shifts to the right and in fact, with the previously undisturbed surface, the current axis was crossed at $-.3$ volt. The same effect may be observed with the other metals, but it is so small as to be practically negligible. Hence it may be stated as a general fact that the apparent initial velocity of emission of electrons is less for old, than it is for new, surfaces in spite of the fact that the new surfaces are more electro-positive than the old. The effect is due in part to the electrons liberated from the receiving electrode by light of the higher frequencies reflected from the illuminated

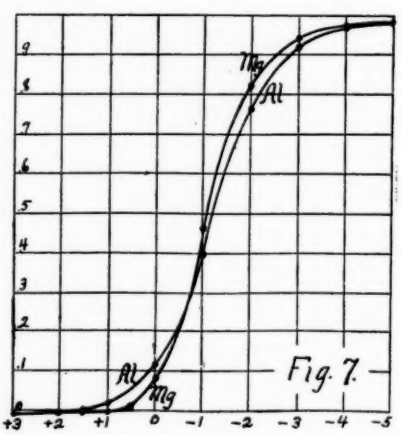


Fig. 7.

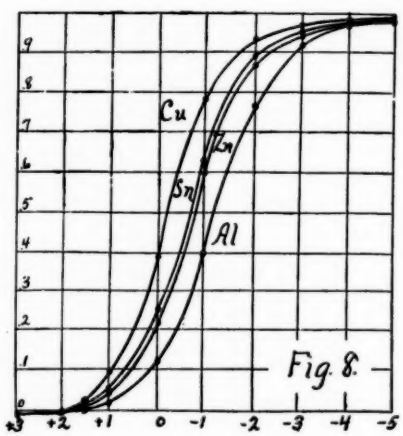


Fig. 8.

surface. This is because the old surfaces are less photo-sensitive than the new, while the number of electrons due to reflected light is practically the same for both and hence the point at which the axis of zero current is crossed by the distribution of velocity curves is further to the right with old than with new surfaces. It seems certain, however, that the film acts also as a mechanical barrier to the passage of electrons from the metal, for the shift of the curve, in the case of magnesium at least, is greater than can be accounted for by the action of electrons liberated from the receiving electrode.

Pushing further the comparison of the magnesium curve with those of the other metals, it will be seen from Fig. 7 that the magnesium curve rises more abruptly than the aluminum curve, crosses the latter and again meets it by turning more abruptly upon approaching the maximum. As stated before, this was a surface a few hours old. With a newer surface, the curve may be wholly to the right of, and approach

more nearly the same general shape as, that for aluminum. On the other hand, with an older aluminum surface the curve approaches the general shape of that for magnesium here shown. These facts also indicate that the film must be considered as a sort of barrier to the passage of electrons from the metal and as exhibiting a contact potential and photo-electric properties of its own which are superimposed upon, or screen off in part, those of the metal beneath.

TABLE VII.

Metal.	Contact P. D.'s.	Apparent Positive Potentials.
Silver	+.024	1.92
Magnesium	+.782	.82
Zinc	+.543	1.75
Aluminum	+.967	1.83
Tin	+.320	1.74
Iron	+.225	1.90
Brass	+.222	1.75
Copper	−.042	1.87

Table VII. gives in the first column the contact potentials of the several metal surfaces against the movable brass plate when the observations for these curves were made. The second column gives the values of the apparent positive potentials acquired by the metals when the disk to be examined was placed in communication with the electrometer and when the wire gauze cylinder previously used as receiving electrode was earthed. These apparent positive potentials are in fair agreement with those indicated by the curves in Figs. 3–8.

Considering all the curves together, it is seen that they tend to emerge from a more or less common point spreading out fan-like at first and later assuming approximately the same general shape, and that the order thus assumed by the metals is that of their contact potentials. The latter fact furnishes substantial evidence that the differences in the applied potentials necessary to produce the saturation current coincide in a general way with those in the observed contact potential differences. That this should be so is more readily explained by assuming that inherent physical properties of the metals rather than chemical action are coming into play.

THE RELATIVE PHOTO-SENSITIVENESS OF METALLIC SURFACES.

It has been stated that the photo-sensitiveness of the newly prepared metallic surfaces is greater than it is for older surfaces. Observations on the photo-sensitiveness of the metals were made both before and

after scraping in order to determine, not only the difference in sensitiveness of new and old surfaces but also the relative sensitiveness of the series of metals, with a view to ascertain if it be related to the contact series. The first column of results in Table VIII. gives the relative photo-sensitiveness of the old unscraped surfaces. It is seen that silver was the most and magnesium the least sensitive of the eight metals, and that the order is not at all that of their contact potentials. (See first column, Table II. or III., for contact potential differences of the old undisturbed surfaces.) In the second and fourth columns of Table VIII. are given two series of results showing the relative sensitiveness of comparatively new surfaces, two days and one day respectively after scraping, and the third and fifth columns give the relative sensitiveness of the metal surfaces just as soon after scraping as observations could be made.

TABLE VIII.

Metal.	Relative Photosensitiveness.				
	Old Original Surfaces.	New Surfaces.			
		I.		II.	
		Before Scraping.	After Scraping.	Before Scraping.	After Scraping.
Silver	28	34	51	32	45
Magnesium	4	28	1000	42	1000
Zinc	5	49	78	53	87
Aluminum	7	190	470	260	560
Tin	19	42	69	45	72
Iron	10	38	65	46	67
Brass	17	34	46	30	45
Copper	13	40	62	40	58

(See second column, Table V.—contact potential differences of the metals just after scraping, and the third and fourth columns, those one day and two days later.) With the newly scraped surfaces magnesium is by far the most photo-sensitive just as it is the most electro-positive. Its photo-sensitiveness is taken as the base for comparison and is for convenience given a value of 1,000. With the newly scraped surfaces the order of the metals, with the single exception of brass, is seen to be exactly that of the contact series. Any given order does not long persist, however, because the aging of the various surfaces proceeds at relatively widely different rates. Thus magnesium, which is at the head of the list directly after scraping, finds its place at the bottom in two days.

It is known that the highly electro-positive metals, sodium and potassium, are exceedingly sensitive to light. There is not wanting evi-

dence, therefore, that the photo-sensitiveness of clean metallic surfaces is related to their contact potentials.

CONCLUSIONS.

The point of view that the so-called contact potentials are due to intrinsic properties of the metals finds substantial support on the basis of the results of this investigation. The considerations leading to this conclusion may be briefly stated as follows:

1. The metals become more electro-positive when new surfaces are prepared in the best obtainable vacuum.

2. The changes in contact potential differences which are observed to take place in film-coated surfaces subjected to photo-electric treatment are such as to indicate that whatever the modifications are, they take place in the film and not in the metal.

3. The observed initial velocities of emission of electrons from recently prepared surfaces are nearly the same for all metals, suggesting that the more electro-positive a metal is, the greater the actual velocity of emission of electrons from its surface.

4. The apparent initial velocities of electrons are less for film coated than for clean surfaces and not in a manner to be accounted for by accompanying changes observed in the contact potentials. To the extent that this is not explained by the differences between the relative effects of the direct illumination and the electrons set free by reflected light for the new and old surfaces, the film acts as a mere mechanical obstruction in addition to serving as an electric screen or contributing to the electrical field.

5. The fact that the differences in the applied accelerating potentials necessary to produce the saturation currents from clean metallic surfaces under illumination coincide in a general way with those in the observed contact potential differences would not be cited as evidence in favor of an electrolytic or chemical theory of contact potentials.

6. Since the photo-sensitiveness of the metals is much greater with new than with old surfaces, and since the order assumed by metals with clean surfaces is practically that of the contact series, it appears that the electro-positive character of a pure metal is an index of the readiness with which it gives up electrons.

A comprehensive view of the above considerations shows that the facts not only warrant the suggestion that the contact potentials are manifestations of inherent properties of the metals, but also throw some light on what the nature of these properties may be. None of the facts are contradicted by supposing that the electro-positive or electro-negative

character of the metal has to do with its ability to retain electrons or its tendency to discharge them. This is essentially the view held by Helmholtz, who conceived of the metals as having specific attractions for positive and negative electricities, the nature and intensity of the electrification displayed by a given metal representing the difference between its attractions for the two kinds.

I take this opportunity to thank Professor Millikan for his counsel and encouragement at all stages of this research and to acknowledge my indebtedness to Mr. Julius Pearson, the mechanician at the Ryerson Physical Laboratory, whose ingenuity and skill made it possible for me to realize and to put into successful operation the apparatus designed for this work.

RYERSON LABORATORY,
THE UNIVERSITY OF CHICAGO,
December, 1913.

ON THE NATURE OF THE VOLTA EFFECT: A REJOINDER.

BY ALBERT E. HENNINGS.

THE only issue which is involved in "A Critique and Study on the Nature of the Volta Effect,"[1] so far as the results of Sanford's experiment[2] are concerned, is whether the contact charge observed on an insulated conductor, such as a ball, when it is moved from a position in which it makes contact with the inside of a hollow earthed conductor, such as a beaker, to a point wholly outside the latter depends upon the outside or the inside surface of the beaker. Sanford believes he has shown that this charge depends on the nature of the *outside* surface of the beaker. The results presented in the "critique" furnish abundant evidence that the charge observed under these conditions depends in no way on the outside surface, but only on the *inside* surface of the beaker. It was pointed out that in Sanford's arrangement the inductive effects of a static charge on the silk cord used were so great as to mask in a large measure the Volta effect itself. His results are therefore such as to invalidate any conclusion which may be arrived at by using them as a basis for argument. In a "reply"[3] to the "critique" Sanford, by refusing to admit that his results are untrustworthy and asserting that the essential elements of the experiment described by him were not reproduced in my work, implies that my results rather than his are to be considered spurious and that my experimental arrangement is incapable of giving the information desired. The situation thus created is not a happy one, for it leaves a fundamental issue apparently undecided. It seems necessary therefore that the evidence in support of my contentions be more convincingly brought out and that the results and arguments about which question has arisen be examined more carefully than was considered desirable in the "critique."

Two alternative hypotheses in regard to the nature of the Volta effect are offered by Sanford in his original paper, and a "still more crucial experiment" is announced by him which will make it easy to choose between them. The experiment consists in observing the charge dis-

[1] PHYS. REV., N. S., Vol. II., p. 1, July, 1913.
[2] PHYS. REV., XXXV., p. 484, December, 1912.
[3] PHYS. REV., N. S., Vol. II., p. 495, December, 1913.

played by an insulated zinc ball after it has made contact with the inside of an earthed copper or aluminum beaker. The conditions were varied by placing discs of tinfoil in the bottom and by completely covering the outside with tinfoil. The attempts made by Sanford to observe the charge taken from the beaker by the ball were made solely to determine whether it is the *outside*, or whether it is the *inside* surface of the beaker upon which this charge depends. Herein then, lies the real issue not only because Sanford's choice between his two hypotheses had to be made on the basis of the observed results, but also, and chiefly, because we fail to agree on what the *true* results are. That we should differ so widely as we do makes it imperative that we inquire whether our experiments as designed and performed are essentially different or inherently incapable of furnishing the information desired and whether the results as observed may not be rendered untrustworthy by causes of an extraneous nature.

My final experimental arrangement, it is true, differed somewhat from that adopted by Sanford, but in its initial stage my experiment took the *exact* form that Sanford's did. A few details only were modified. The single feature added was that of enclosing the whole apparatus in a cage of wire netting. As I reported in the "critique," I did not succeed, when using Sanford's identical arrangement, in confirming his results and found moreover that the silk thread used to insulate and operate the ball was the seat of an electrical charge the inductive effects of which were so great as to mask in large measure the Volta effect itself. That the existence of such a charge is an annoying fact may be demonstrated to the complete satisfaction of any one who may have entertained the idea that it is purely hypothetical by bringing a bit of silk or any of the ordinary insulators on the end of an earthed wire toward an insulated conductor which is in communication with an electrometer. The magnitude of the induced charge which may be thus almost invariably observed is surprising as well as convincing. The persistence of such charges and their inductive effects rendered Sanford's particular arrangement incapable of yielding correct or consistent results.

While the slight modification in the experimental proceedure then adopted requires no justification, it may be instructive nevertheless to consider briefly the *essential elements* of the experiment. Which of two conductors, A, and B, is the more electropositive may be determined as follows: Let A be placed upon an insulating stand and let B, to which is attached an earthed wire, be brought near and in contact with A. Both A and B are now in communication with the earth. If B is then removed by means of the earthed wire attached to it, A will display

either a positive or a negative charge. Suppose this charge is negative. Again let A and B be in contact with each other but communication with the earth being this time effected by a wire attached to A. If now B is removed by means of an uncharged insulator (such as a silk thread is not likely to be) attached to it, the charge on B will be positive if the one previously displayed by A was negative. In the absence of disturbing causes there is no choice to be made between the two procedures. They are essentially the same and each gives equally well the relative position of the metals in the contact series. To decide the issue about which the discussion centers it is necessary to ascertain merely the character of the electrical transfer between ball and beaker. The fundamental conditions are the same as for the conductors A and B, above. If the ball exhibits a *positive* charge when removed from contact with the inside of the earthed beaker, then the beaker, placed upon an insulating stand, displays a *negative* charge when the earthed ball is moved away from its inner surface. The electrical transfer which takes place is relatively the same in each case. Since the two procedures are therefore virtually identical, the assertion that in one there are reproduced none of the essential elements of the other is an ill-advised one.

In his criticism of my arrangement of a metallic beaker connected to earth by the contact between it and the ball to which is attached an earthed wire, Sanford raises the objection that this wire leading as it does from the inside of the beaker into the space surrounding it outside, becomes itself exposed, and consequently exposes the inside of the beaker also, to the induction of surrounding charges. It is to be remembered that my apparatus was completely enclosed in a large cage of earthed wire netting so that any possible disturbing charges must have been inside the cage. Moreover the insulating parts of the apparatus were also carefully screened by earthed conductors, so that it is impossible that any such charges could create disturbances of so pronounced a character as to make it doubtful whether or not it was the Volta effect which was really observed. The only possible objection to the wire attached to the ball is that it does contribute something to the transfer of electricity between ball and beaker by reason of its own contact potential with reference to the inside of the beaker, but its contribution to the general effect is negligible compared to that attributable to the ball not only because the area of that portion of its surface exposed to and within range of the surface of the beaker is relatively very small but also because the distance between the wire surface and the beaker surface is very great compared to the average of that between the mutually exposed parts of ball and beaker. A steel wire was used in my

work however so that, since the ball was one of steel, even this objectionable feature was practically eliminated. Thus, in every conceivable way, the endeavor was made to remove or to reduce to a minimum all disturbing elements so that it was the true Volta effect that was actually observed. Hence it may be legitimately claimed that the results reported in the "critique" are incontestible and therefore establish firmly some of the significant facts in regard to the nature of the Volta effect.

A critical examination of Sanford's results as he has recorded them shows that they cannot be accepted as representing observations on the true Volta effect. In the first of the tables which he gives, the mean deflection of the electroscope for two series of ten observations each, when the zinc ball shares its charge with the electroscope after having made contact with the inside of the earthed beaker, is 14.2 scale divisions in the case of the copper beaker and 35.0 scale divisions in the case of the aluminum beaker. Since the sensitiveness of the electroscope was 10 divisions per volt this gives an apparent contact difference of two volts between aluminum and copper. However, this does not represent the true contact difference nor did Sanford wish it to be considered so. But obviously these mean deflections represent the relative intensities of charges of the same sign. One would expect however the contact charges in the two cases to be of opposite sign since zinc is ordinarily electropositive to copper and electronegative to aluminum. It is not impossible for zinc to be electropositive to aluminum, but in that case the contact charge should have been less in the case of the aluminum beaker than in the case of the copper beaker, for it would be a most unusual situation in which copper is electropositive with reference to either aluminum or zinc. The illogical nature of these results can be explained however by the presence of a static charge of positive sign with reference to the metals upon the silk cord. The effect of this would be to give the ball a negative charge by induction. This induced charge is likely also to be large compared to the true contact charges. The negative charge observed on the ball is the resultant of this induced charge and that due to the contact effect. Now if the zinc is electropositive to copper and electronegative to aluminum, the resultant negative charge on the ball when contact is made with the beakers is less with the copper than with aluminum. It is seen therefore that the "hypothetical" charge on the silk cord explains in part at least the illogical nature of the results presented by Sanford. Of course other disturbing causes may have been present also for he states that he made no attempt whatever to eliminate any of the electrostatic disturbances which are always to be contended with in work of this kind.

The same sort of inconsistencies appear in the results in the other tables. Disturbing causes were therefore undeniably present so that it is not surprising that the results should lead to erroneous conclusions if they be interpreted as representing only the Volta effect.

Sanford considers himself fortified against an attack on the validity of his conclusions because his final statement of what he conceives to be the teachings of his experiment is in apparent agreement with one of the statements which he quotes from the "critique." Now his conclusion was reached by choosing between the two hypotheses which he offered, but the erroneous character of his results led him to reject the one which the true results would have forced him, if his reasoning were logical, to accept. Furthermore, in laying the foundation for the second of his hypotheses, the one he accepted, Sanford explicitly assumes that the potential of the inside of a hollow conductor is the same as that of the outside. This may not be true except when the outside and inside surfaces are of the same metal, for in the case of an earthed copper beaker covered on the outside with tinfoil, the copper and the tinfoil surfaces act as though they each have their own characteristic potentials with reference to the earth. In making this assumption Sanford has committed the error of setting up a condition in his hypothesis which contradicts the very conclusion which he reaches by means of it. Thus it is that erroneous results and an unsound hypothesis have led to what seems to be the correct conclusion.

We are here concerned not with an ultimate theory of the Volta effect but with one of the fundamental facts which must be reckoned with in the formulation of such a theory. My experiments show—and in this they are in direct opposition to Sanford's—that "the Volta effect depends under all circumstances on the nature of the *opposing* surfaces of conductors which have been brought near, or in contact with, each other. Indeed it depends *only* on the surfaces exposed to, and within range of, each other. All, and only, such surfaces, or portions of surfaces, of conductors contribute to the general effect."[1]

UNIVERSITY OF SASKATCHEWAN,
April, 1914.

[1] PHYS. REV., N. S., Vol. II., p. 15, July, 1913.

PHASE RELATIONS IN THE ACOUSTIC SHADOW OF A RIGID SPHERE; PHASE DIFFERENCE AT THE EARS.

BY G. W. STEWART.

SATISFACTORY explanations of the many phenomena in sound localization can be realized only after the bases are laid for a successful discrimination between physical and psychological factors. The experiment in localization which seems to be the most difficult of explanation is that first noted by Rostosky,[1] independently reported by Rayleigh[2] and afterward studied by Rayleigh,[3] More and Fry,[4] Myers and Wilson[5] and More.[6] These experiments show that there is an illusion of localization if there are produced at the ears various differences in phase obtained from the same source or from sources of the same frequency. If the difference in phase is 0°, the sound appears directly in front. If the difference is 90°, and the phase of the right ear is leading, the sound appears to be on the right side. When the difference becomes 180°, the sound appears in front or in the rear, and when the difference is 270° the sound is at the left. Finally, at 0° phase difference the sound appears in front. These points are not the only ones, for, as a matter of fact, the sound seems to pass continually about the head, internally or externally, from one of the points to the other. These results are only a portion of those obtained with varying phase differences, but they are sufficient to show that an understanding of the varying phase differences produced at the ears by a rotation of the head, the source of sound being at a given distance, is needed, for it would be a distinct assistance in a discussion of the influence of a difference in phase at the ears.

A brief extension of a theory already published[7] will give the desired information. Let the source be confined to a small area on the face of a rigid sphere, and let the velocity of this source region be harmonic with the same magnitude throughout.

[1] Philosophische Studien, 19, 1902, p. 557.
[2] Phil. Mag., 13, 1907, p. 214.
[3] Phil. Mag., 13, 1907, p. 316, and Proc. Roy. Soc., London, *A* 83, 1909, p. 61.
[4] Phil. Mag., 13, 1907, p. 452.
[5] Proc. Roy. Soc., 80, 1908, p. 260, and Brit. Jl. of Psych., 11, 1908, p. 363.
[6] Phil. Mag., 18, 1909, p. 308.
[7] G. W. Stewart, PHYS. REV., XXXIII, No. 6, 1911, p. 467.

ψ represents the velocity potential.
a represents the velocity of sound.
r represents the distance from center of sphere.
c represents the radius of the sphere.
dS represents an element of surface.

$$k = \frac{2\pi}{\text{wave length}},$$

$$\gamma = k(at - r + c),$$

$$F = \Sigma \frac{2n+1}{2} P_n(\mu) \frac{\alpha\alpha' + \beta\beta'}{\alpha^2 + \beta^2},$$

$$G = \Sigma \frac{2n+1}{2} P_n(\mu) \frac{\alpha\beta' - \alpha'\beta}{\alpha^2 + \beta^2}.$$

α, α', β and β' are defined in the article cited. Then

$$\dot{\psi} = \frac{ka}{2\pi r} (F \sin \gamma + G \cos \gamma) \iint Uds. \tag{1}$$

The condensation s is related to $\dot{\psi}$ by the following

$$s = -\frac{\dot{\psi}}{a^2}, \tag{2}$$

where s is related to the densities by the equation $\rho = \rho_0(1 + s)$.

Substituting (1) in (2) we have

$$s = -\left[\frac{k}{2\pi ra} \iint Uds\right] \sqrt{F^2 + G^2} \cos(\gamma - \epsilon), \tag{3}$$

if $\epsilon = \tan^{-1} F/G$.

$\iint UdS$ is the surface integral over the source region of the maximum value of the velocity U, and is therefore independent of r, t, and μ, or the cosine of the angle between lines joining the center of the sphere with the source of sound and the selected point. F and G vary with r and μ. Given a value r, *i. e.*, points on a concentric sphere, the maximum values of s will change with values of $\sqrt{F^2 + G^2}$, and at any given time the phase of s will vary from point to point on this sphere with values of ϵ, γ varying only with the time. Differences of phase can therefore be readily found by obtaining the different values of ϵ.

When these phase differences are ascertained, it is not difficult to obtain the phase differences on the sphere with the source at a distance r. For according to the Helmholtz reciprocal theorem,[1] if the source is at A, the resulting velocity potential at a second point B is the same both in *magnitude* and *phase* as it would have been at A, had the source

[1] Rayleigh, Theory of Sound, Vol. II., p. 145.

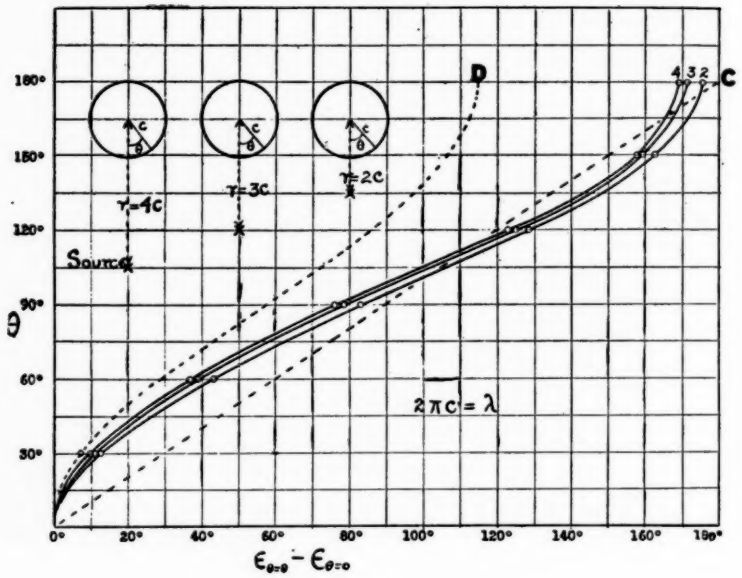
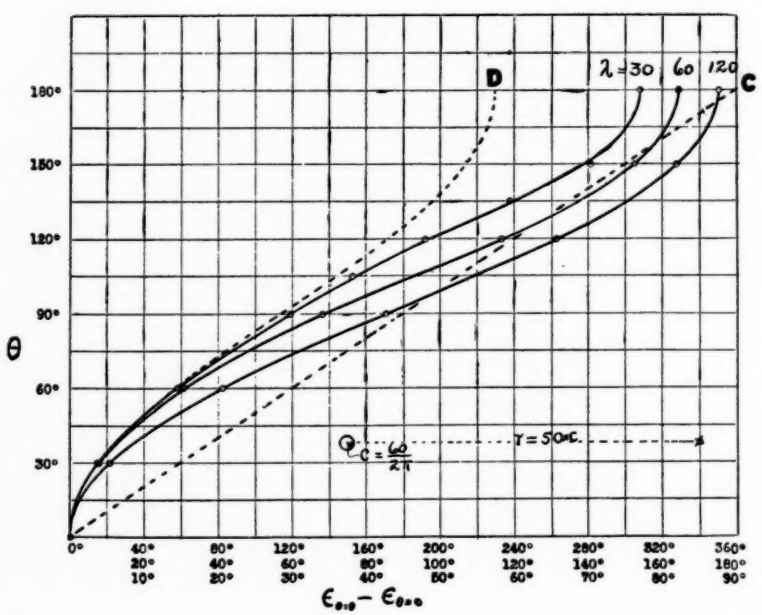

D
C
4 3 2
180°
150°
120°
90°
60°
30°
θ
Source
r=4c
r=3c
r=2c
2πc=λ
0° 20° 40° 60° 80° 100° 120° 140° 160° 180°
ε_{θ=θ} − ε_{θ=0}

Fig. 1.


D
C
λ=30 60 120
180°
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θ
c=60/2π
r=50c.
0° 40° 80° 120° 160° 200° 240° 280° 320° 360°
20° 40° 60° 80° 100° 120° 140° 160° 180°
10° 20° 30° 40° 50° 60° 70° 80° 90°
ε_{θ=θ} − ε_{θ=0}

Fig. 2.

of sound been at B. According to (2), the same reciprocal relation holds for the condensation s. Hence (3) will be used for the case where the source is at a distance r and the phase relations are desired on the rigid sphere itself.

Results.

We desire to know the variations of phase for positions on the sphere from 0° to 180° where these are taken on any great circle with 0° at the point nearest to the source which is at a distance r from the center of the sphere. The necessary computations for values of F and G are very laborious and consequently the conditions chosen were determined by

Table I.

Wave-length $= 2\pi c$.

θ	Distance $r=2c$.		$r=3c$.		$r=4c$.	
	F and G.	$\epsilon_{\theta=\theta}-\epsilon_{\theta=0}$	F and G.	$\epsilon_{\theta=\theta}-\epsilon_{\theta=0}$	F and G.	$\epsilon_{\theta=\theta}-\epsilon_{\theta=0}$
0°	+1.4646	0.0°	+1.0573	0.0°	+0.9232	0.0°
	+0.2571		+0.2566		+0.2506	
30°	+1.1123		+0.9349		+0.8556	
	−0.0496	12.51°	+0.0451	10.88°	+0.0778	9.99°
60°	+0.5389		+0.5909		+0.6018	
	−0.3531	43.19°	−0.2796	38.97°	−0.2376	36.72°
90°	+0.1111		+0.1816		+0.2184	
	−0.3648	83.03°	−0.3878	78.45°	−0.3912	76.00°
120°	−0.1315		−0.1193		−0.1086	
	−0.2401	128.64°	−0.3040	125.07°	−0.3374	123.02°
150°	−0.2399		−0.2708		−0.2880	
	−0.1244	162.54°	−0.1823	159.69°	−0.2190	157.83°
180°	−0.2629		−0.3131		−0.3402	169.28°
	−0.0717	174.70°	−0.1300	171.10°	−0.1652	

values that had already been obtained in other work. These are, however, sufficient to indicate what is to be anticipated in the case of various frequencies and distances from the sphere. The accompanying tables, I. and II., give the numerical values. The accompanying curves, Figs. 1 and 2, present the results with sufficient clearness, but the tables are necessary in order to make a more traceable record. In Table I. and Fig. 1 the distance is varied. The results are obviously applicable for any value of c, the wave-length always being equal to the circum-

ference of the sphere. In the case of the head, the circumference may be taken as 60 cm. In Table II. and Fig. 2 the numerical value for c is chosen with special reference to the head as the sphere, but the results would hold for any sphere if the relative values of wave-length, circumference and distance are retained.

TABLE II.

$r = 477$ cm. $c = 60/2\pi$

θ	Wave-Length, 120 cm.		60 cm.		30 cm.	
	F and G.	$\epsilon_{\theta=\theta}-\epsilon_{\theta=0}$	F and G.	$\epsilon_{\theta=\theta}-\epsilon_{\theta=0}$	F and G.	$\epsilon_{\theta=\theta}-\epsilon_{\theta=0}$
0°	+0.5371		+0.6830		+0.7737	0.0°
	+0.1499	0.0°	+0.2320	0.0°	+0.2016	
30°	+0.5346		+0.6800	7.87°	+0.7803	15.06°
	+0.0966	5.34°	+0.1308		−0.0062	
60°	+0.5077		+0.5899		+0.5097	58.04°
	−0.0447	20.60°	−0.1215	30.42°	−0.4826	
990°	+0.4280	42.81°	+0.3149		−0.1478	119.37°
	−0.2201		−0.3665	68.10°	−0.5609	
105°					−0.3638	152.27°
					−0.3314	
120°	+0.3060	65.62°	−0.0599		−0.3879	191.75°
	−0.3650		−0.4307	116.68°	−0.0194	
135°					−0.2378	237.19°
					+0.1359	
150°	+0.1955	81.96°	−0.3367		−0.0235	281.27°
	−0.4467		−0.3522	152.37°	+0.4026	
180°	+0.1517	87.73°	−0.4297		+0.2131	308.14°
	−0.4708		−0.2959	164.21°	+0.4892	

In both figures $\epsilon_{\theta=\theta} - \epsilon_{\theta=0}$ represents the phase difference between the point $(c, \theta = 0)$ and all points $(c, \theta = \theta)$, the straight line C gives the differences of phase that would occur if the condensation travelled around the circumference with the velocity of sound, and the curve D indicates the variation in phase that would occur along the diameter if the sphere were absent. The same accuracy does not hold for all the results. Those for a wave-length of 120 cm. in Fig. 2 and those of Curves 2 and 3 in Fig. 1 are very accurate, but the computations for the three other curves have not been so carefully checked. Values for 105°

and 135° were introduced to assist in locating the correct curve with the wave-length 30 cm.

Attention might be called to several points of interest.

1. The effect of increasing distance is small.

2. The phase changes the most rapidly in the neighborhood of the portion designated by 90°–120° in Fig. 1.

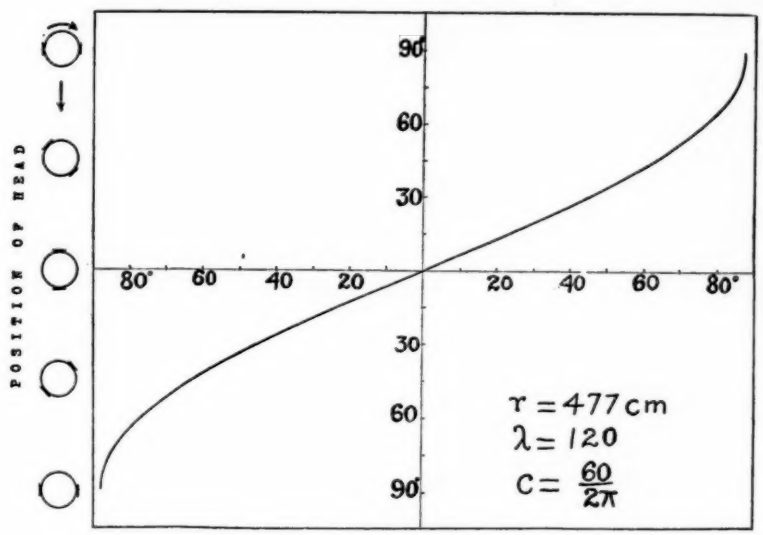

Fig. 3.

3. In most of the curves shown, in a portion of the region designated by $120° < \theta < 180°$ in Fig. 1, the phase differs from that at 0° by an amount in *excess* of what would occur if the sound travelled directly up to the point $\theta = 0°$ and then followed the surface of the sphere with the velocity of sound. This is a surprising result, if one does not give thought to the fact that the condensation is a resultant.

4. The interesting result just stated does not exist with the wave length 30 cm. That this should be the case appears reasonable when one considers that the effective wave front is not so large with the smaller wave-lengths.

5. The difference of phase is relatively less with the decreasing wave length.

Difference in Phase at the Ears.

The difference in phase at the ears can readily be obtained from the preceding results if one supposes the head to be a rigid sphere with the

ears diametrically opposite. The results for the case of wave length 120 cm., sphere circumference 60 cm. and distance of sound 477 cm. from the center of the sphere, are given in accompanying Fig. 3. The phase difference changes the most rapidly when the source of sound is in front or behind the hearer. These results give an estimate of the physical aspect of phase differences at the ears.

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THE TIME FACTOR IN SELENIUM RESISTANCE.

By G. E. Grantham.

EARLY observers of the light action of selenium discovered that the electrical resistance of selenium does not reach an equilibrium value instantaneously after exposure to light, and that the rate of change of resistance on exposure is much greater than the recovery rate.

A large amount of material has been published showing the relation between time of exposure and the resistance of the selenium cell;[1] and the effects of various agencies, such as pressure,[2] wave length of light to which the selenium was exposed,[3] temperature of the cell,[4] Röntgen radiation,[5] etc. A few observers have investigated the recovery of the selenium cell during the fractional part of a second following exposure. Since this field has not been entirely covered by experiment the present work was undertaken.

The problem suggested the use of a rotating disk from which sectors had been cut to allow the light to fall upon the cell, the cell to be in one arm of a Wheatstone bridge with some device for connecting a galvanometer in the bridge circuit at a known time interval after exposure. This method introduced the necessity of a preliminary experiment to determine the effects of different speeds of the disk on the change of resistance of the cell.

Preliminary Experiment.

A selenium cell, connected in one arm of a Wheatstone bridge, was placed in a light-tight box, the inside of which was coated with lampblack and shellac. A piece of iron pipe of 5 cm. diameter and 60 cm. long was fitted closely in a hole in one end of the box. A cap which had an opening in it the exact size of one of the sectors was placed over the outer end of the pipe. The rotating disk of 45 cm. diameter was mounted at right angles to the pipe on a shaft to which was attached a speed counter and a small electric motor. Two sectors diametrically opposite were cut from the disk permitting the cell to be exposed twice each

[1] F. C. Brown, Phys. Rev., XXXII., p. 252; XXXIII., p. 406, 1911.
[2] F. C. Brown and Joel Stebbins, Phys. Rev., XXVI., p. 273, 1908.
[3] Pfund, Phys. Rev., XXVIII., p. 324, 1909.
[4] Miss Louise MacDowell, Phys. Rev., XXXI., p. 529, 1910.
[5] G. Athanasaidis, Ann. d. Physik, 27.4, p. 890.

revolution. The disk was rotated at 215, 690 and 1,200 R.P.M. A one candle power incandescent lamp was placed near the disk and used as the source. The result of these observations is shown graphically in Fig. 1.

The preliminary experiment showed that there was a variation in the resistance of the cell with change of speed of the disk, although the quantity of light falling upon the cell was the same at all speeds. However, this change of resistance was so slow that it could not interfere essentially with the observations taken by the proposed method.

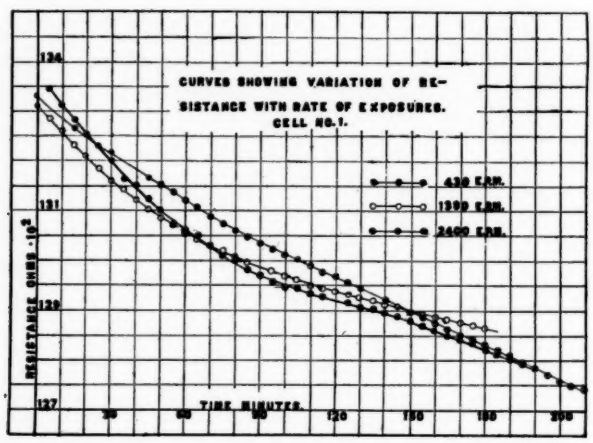

Fig. 1.

Exposures made to a 1 c. p. incandescent lamp.

The apparatus constructed for the study of the resistance change during a short interval was as follows: A small hard rubber disk of 5 cm. diameter and a metal disk of 45 cm. diameter were mounted on the same shaft of a motor equipped with a speed counter. In the circumference of the rubber disk, 90 degrees apart, were inlaid four brass cylinders of 0.8 cm. diameter. The dia netrically opposite cylinders were connected in pairs by brass strips on the side of the disk. Two brushes were mounted on a wooden block which was separate from the remainder of the apparatus and yet free to rotate about the same axis as the disk. A pointer attached to the axis of the brushes moved over a fixed graduated disk and served the double purpose of indicating the angle of lead or lag of the brushes with respect to the sectors and of clamping the brushes in any desired position. The brushes were connected in the galvanometer circuit of a Wheatstone bridge. The two galvanometers used at different parts of the study were of the d'Arsonval type, one having a figure of merit of 0.83×10^{-9} amperes per mm. for a distance of

212 cm. between the scale and mirror. The other was not as sensitive. A single storage cell was used as the battery. The selenium cell was placed in the light-tight box previously described and connected in the Wheatstone bridge circuit.

The selenium cell used in the preliminary experiment was one of the Bidwell type[1] bought from Max Kohl and will be designated as Cell No. 1 throughout this paper. Three selenium cells were used for the second part of the experiment. Cell No. 1 had a sensitiveness of 1.0 : 1.5 (ratio of change of resistance to dark resistance). Cells *22B* and *50C* were made by Giltay. The sensitiveness of *22B* was 1.0 : 1.4 and that of *50C* was 1.0 : 2.2. The dark resistances of Nos. 1, *22B* and *50C* were 35,000, 290,000 and 20,000 ohms respectively. The cells frequently became almost insensitive. By connecting a cell in series with two spark gaps, two Leyden jars in multiple and a 3 in. spark induction coil and sending oscillatory discharges through the cell for about five minutes the sensitiveness was generally restored. The cell would be in a very unsteady state of equilibrium for a day following such treatment.

For illumination a Nernst lamp, the terminals of which were kept at a constant voltage, was used for a part of the experiment and a Welsbach burner for the remainder.

METHOD OF TAKING OBSERVATIONS.

The apparatus was so arranged that when the indicator on the graduated circle pointed to zero the galvanometer was thrown in the circuit at the same instant as that at which light fell upon the cell. If the indicator pointed to 10 degrees, the galvanometer was thrown in the circuit at a time later than the exposure equal to the time required for the disk to rotate through 10 degrees. The speed of rotation was given by the speed counter and this time interval was easily calculated. A separate switch served the purpose of throwing the commutator out of the bridge circuit. The brush contacts were tested in this manner.

RESULTS.

The relation between time and resistance for the preliminary experiment is shown in Fig. 1. It is seen that during the first hour the rate of change of resistance increased with the speed. For a speed of 215 R.P.M. the resistance change during the first hour was 210 ohms, for a speed of 690 R.P.M. the change was 260 ohms, and for a speed of 1,200 R.P.M. the change was 310 ohms. During the remainder of the time the cell approached the equilibrium resistance. This equilibrium

[1] Shelford Bidwell, Proc. Phys. Soc., London, Vol. XI., p. 61.

resistance is the resistance of the cell at the time that the decrease on exposure is just equal to the increase in the dark. It is evident from the

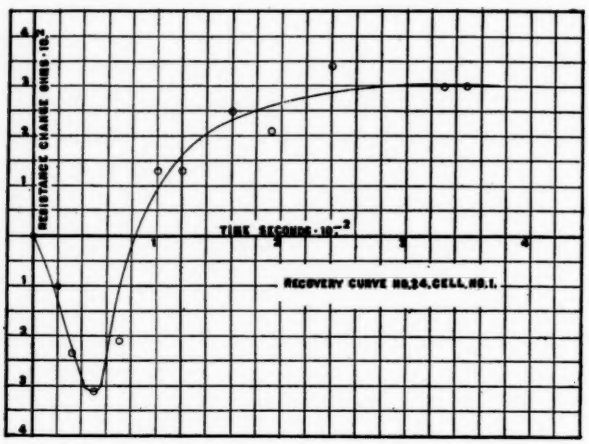

Fig. 2.

Exposures made to a Nernst lamp at a distance of 60 cm. Speed of disk, 490 R.P.M.

curve that the equilibrium resistances will not be equal although the total quantity of light falling upon the cell is the same.

Figs. 2 to 5 show the results of the experiment proper. The loops in curves below the X axis apparently indicate that the resistance of the

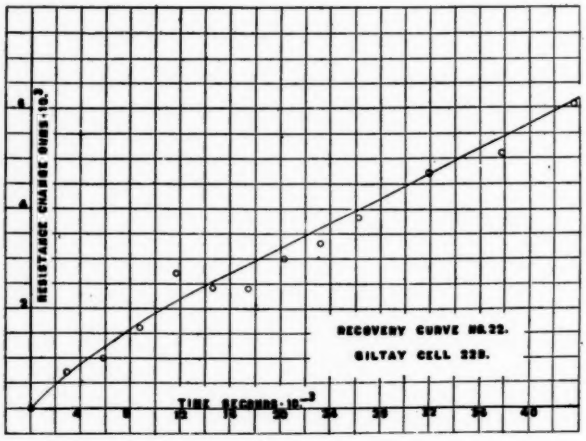

Fig. 3.

Exposures made to a Welsbach burner at a distance of 70 cm. Speed of disk 560 R.P.M.

cell a short time after exposure was less than the resistance when the cell was actually exposed to the light. It was first thought that this

negative loop might be caused by some contact electromotive force at the brushes and an auxiliary experiment was performed by substituting for the hard rubber disk a commutator made of two brass rods set at right angles to each other. Brushes made of the same material as the commutator were used. Then a resistance of the same magnitude as that of the selenium cell was introduced in the circuit, by reversing a switch which at the same time cut the selenium cell out of the circuit. No negative loop appeared and it was concluded that the loop was due to some change within the cell.

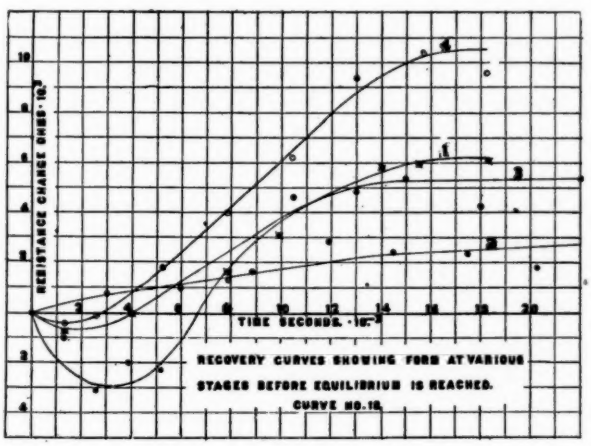
RESISTANCE CHANGE OHMS · 10³
TIME SECONDS · 10⁻²
RECOVERY CURVES SHOWING FORM AT VARIOUS
STAGES BEFORE EQUILIBRIUM IS REACHED.
CURVE NO. 1.

Fig. 4.

Exposures made to a Welsbach burner at a distance of 70 cm. Speed of disk for curves Nos. 1, 2, 3 and 4, 1200, 560, 1250 and 2400 R.P.M. respectively.

The negative loop did not appear if the readings were obtained within a very short time after the first exposure, as shown in Fig. 3. If the motor was run for an hour or longer before the readings were taken, a pronounced negative loop was obtained, as shown in Fig. 2. Fig. 4 shows some of the many various forms of curves obtained. Curve No. 1 was obtained when the cell had reached its equilibrium value.

Discussion of Results.

The results of this experiment can be explained if it be assumed[1] that selenium consists of three components, A, B, and C, which under the action of light change according to the reaction; $A \rightleftharpoons B \rightleftharpoons C$. Assume that the resistivity of the component A is infinite, that of B approaches the resistivity of metals, and that of C has a value near that of A. Assume, further, that component A changes to B at the rate a_1, B changes

[1] F. C. Brown, Phys. Rev., Vol. XXXIII, p. 1, 1911.

to C at the rate b_1, that the respective reverse rates are a_2 and b_2, and that the rate a_1 is much greater than the rate b_1. Then for a very short exposure some of A changes to B, but very little of B changes to C. During the recovery period between exposures, which is approximately thirty times as long as the time of exposure, some of C will change to B and some of B will change to A, but as the recovery rate is slow compared to the changing rate for one exposure, so for very short repeated exposures there will be a larger transformation to B than for longer repeated exposures. The resistance of the selenium cell depends upon the amount of B present and consequently for a time the rate of change should be greater for short exposures. The differences in the equilibrium values are due to the different amounts of B present.

In accordance with this hypothesis, the negative loop in Figs. 2 to 5 is easily explained. For a single short exposure, A changes to B, but very little of B changes to C. The change of C to B for a single short exposure can be neglected, but for repeated short exposures more and more of B changes to C, so that a longer time will be required for recovery. After the machine has been running for a time, a certain amount of B will change rapidly to C on exposure and then change slowly from C to B in the dark. Obviously there will be an apparent negative change due to the lag of the $B \leftarrow C$ change behind the $B \rightarrow C$ change. The curves of Figs. 2 to 5 then give a difference value between exposure and recovery values.

The equation of the resistance-time curves will have constants depending upon the rates of change a_1, a_2, b_1 and b_2. The conductivity will depend upon the amount of B present and F. C. Brown[1] has shown the relation to be given by the equation

$$i = K(L/N + C_1e^{m_1t} + C_2e^{m_2t}), \tag{1}$$

in which L, N, C, m_1, C_2 and m_2 are constants which depend upon the rates of change of the components. By writing five equations using different values for t the constants may be eliminated. For convenience the substitutions $x = e^{m_1}$ and $y = e^{m_2}$ were made. The final equation then is:

$$\frac{y^2(i_2 - i_1) - (i_4 - i_3)}{y^2(i_1 - i_0) - (i_3 - i_2)} = \frac{y^2(i_1 - i_0) - (i_3 - i_2)}{y(i_1 - i_0) - (i_2 - i_1)} - y, \tag{2}$$

in which i_0, i_1, i_2, i_3, and i_4 are the values of the conductivity at times t_0, t_1, t_2, t_3, and t_4 respectively. By choosing values of x and y the constants for a family of curves may be calculated, giving the various forms of the curves between the equilibrium value of the cell and the condition

[1] Loc. cit.

existing after the first few exposures. The constants for a family of such curves are given in Table I. The equation which most nearly represents curve No. 3 of Fig. 4 was found by a cut and try process to be:

$$i = 1017 + 4005e^{-3\cdot21t} + 4063e^{-2\cdot91t}. \qquad (3)$$

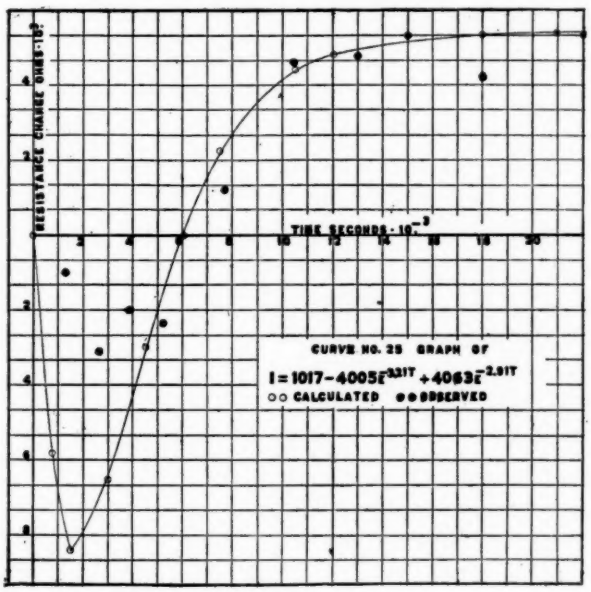

Fig. 5.

Comparison of theoretical and experimental data.

This equation is shown in graphical form in Fig. 5 together with the points experimentally determined. It is seen that beyond four one thousandths of a second the curves are almost identical. No values of

TABLE I.

Values of the Constants upon which the Rates a_1, a_2, b_1 and b_2 depend.

x	y	L/N	C_1	C_2	m_1	m_2
0.0343	0.06	1,017	− 2,121	2,179	−3.4	−2.82
0.0243	0.07	1,017	− 1,188	1,246	−3.74	−2.66
0.0373	0.057	1,017	− 2,788	2,846	−3.3	−2.87
0.0443	0.05	1,017	− 9,666	9,724	−3.12	−3.0
0.0463	0.048	1,017	−32,480	3,253.8	−3.08	−3.04
0.0423	0.052	1,017	− 5,668	5,726	−3.17	−2.96
0.0403	0.054	1,017	− 4,005	4,063	−3.21	−2.92[1]
0.0393	0.055	1,017	− 3,491	3,549	−3.24	−2.9
0.0143	0.08	1,017	− 812	870	−4.33	−2.52
0.0043	0.09	1,017	− 615	673	−7.68	−2.4

[1] Values chosen for equation (3).

x and y which give finite values for the different rates will make the curves compare favorably below four one-thousandths of a second. Then if the general equation for conductivity holds it is evident that the curve should reach a minimum a very short time after exposure. The theory offered explains this. For a very short exposure there will be a change $A \rightarrow B$. Since the rate a_2 is smaller than the rate a_1, if the galvanometer be thrown in the circuit in such a short time following exposure that but little of $A \leftarrow B$ change has taken place, the resistance must be lower than when measured during the exposure, for a_1 is finite and at a speed of 500 R.P.M. the time of exposure is less than one thousandth of a second. The effect of the C component will not enter for every short exposures. Because of the time of contact of the brushes, the time interval following exposures could not be measured to a greater degree of accuracy than two thousandths of a second. This explains why the curves plotted from experimental values do not have a minimum nearer the ordinate.

The results of these experiments are in accord with the three component theory of selenium.

It is intended, in a later paper, to show the variation of resistance of a light-negative cell under similar conditions.

This investigation was suggested by Professor Arthur L. Foley and I wish to thank him for his kindly interest and direction during the course of the experiment. I wish also to thank Dr. R. R. Ramsey for his many helpful suggestions.

PHYSICS LABORATORY,
INDIANA UNIVERSITY.

A STUDY OF THE MAGNETIC QUALITIES OF STRESSED IRON AND STEEL.[1]

BY C. M. SMITH AND GEO. W. SHERMAN, JR.

INTRODUCTION.

IT was the purpose of this investigation to study the effect of stress on the magnetic qualities of iron and steel, using as test pieces short cylindrical bars. In the earlier studies[2] of magnetic properties as affected by stress, the test piece always took the form of a long slender wire; however the material of which the wire is composed is probably greatly modified as to its magnetic qualities by the process of drawing, and so the results obtained on samples of this form may not be at all representative of the material itself.

The chief desideratum in all magnetic testing is to secure results on a given test piece which will be as nearly as possible representative of the material from which the piece was formed, and this is achieved more nearly by those methods which use a short-circuited bar, thus doing away with the effects of polar fields.

The compensated permeameter as designed by Burrows[3] was used in these tests, one of the two test bars being clamped in an Olsen machine, thus making it possible to secure data for normal B–H curves, while the bar was under varying stress conditions.

It has been suggested that some definite relation should be found between the magnetic and elastic constants of steel, and to this end the present study has been directed.

The materials studied were rail steel, wrought iron, mild steel and silicon steel such as is used in transformer plate and for dynamo electric machines.

APPARATUS.

The test pieces were clamped vertically in the testing machine, surrounded by the magnetizing coils of the permeameter as shown in Fig. 1. The general form of the permeameter is shown by Fig. 2.

[1] The experimental work was performed by Mr. Geo. W. Sherman.

[2] Villari, Pogg. Ann., 1868; Kelvin, Phil. Trans., 1879, Vol. 170, p. 55.

[3] Bulletin of the Bureau of Standards, Vol. 6, No. 1, May, 1909.

The magnetizing winding M_t, with an H constant of 105, was wound on a tube of brass enclosing the test bar T. An exactly similar coil M_a surrounds the bar A while the four similar compensating coils M_c, when supplied with proper current, furnish a magneto-motive force sufficient to overcome the reluctance of the yokes and joints, when the circuit is said to be compensated. The coil S_t is the induction or test coil, used in connection with S_a and S_c and a Leeds and Northrup type H galvanometer G_2 to determine the induction density in the test specimen. A six pole mercury reversing switch is used to reverse the magnetizing and compensating currents, and to reverse the terminals of the ammeter in

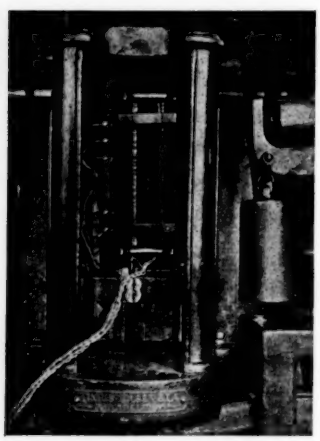

Fig. 1.

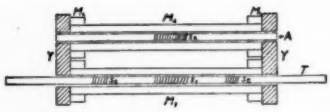

Fig. 2.

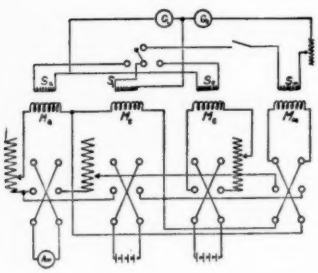

Fig. 3.

the magnetizing circuit. Compensation was effected by the zero method of Burrows, using a galvanometer G_1, of the Leeds and Northrup portable type. The standard of mutual inductance was wound on a marble spool and calibrated at the Bureau of Standards.

THEORETICAL.

The magnetizing field strength is calculated from the formula for the field at the center of a long solenoid

$$F = 0.4\pi ni. \tag{1}$$

The magnetic circuit is not uniform as in the case of a ring, so some modification has to be made. A winding of one hundred turns is placed about the center of the test bars to measure the induction density. A similar coil is placed at the center of the auxiliary bar A. The two coils are placed in opposition inductively, and in series with a ballistic

galvanometer. When the two main magnetizing currents are adjusted so that the galvanometer shows no deflection on reversal, the flux at the center of one bar must equal the flux at the center of the other. Near the end of the test bar are placed two coils of fifty turns each which can be connected additively and in opposition to the test coil at the center.

Burrows[1] has found that if, with this arrangement, a balance again be attained, by sending current through the four end compensating coils and opposing the test coils against the two coils S_e, the magnetic circuit behaved essentially as a perfect magnetic circuit. That is, an exploring coil placed at any point about the circuit will receive the same charge, on reversal of the magnetizing current.

The induction density was determined in the ordinary ballistic manner, and is given by

$$B = \frac{10^8 MiD}{ASd}. \tag{2}$$

M is the mutual inductance,
i is the current through the mutual inductance,
d is the deflection due to the reversal of i,
A is the area of the test bar,
S is the number of turns in the test coil,
D is the deflection due to the reversal of the flux in the circuit.

The above applies only when M is kept constant and D and d are allowed to vary in the usual manner. The zero method worked out by Burrows requires a variable mutual inductance with the two secondary circuits opposed so that D and d neutralize each other and the equation becomes

$$B = \frac{10^8 Mi}{AS}. \tag{3}$$

The zero method is troublesome as there is a difference in the time constants of the two circuits and it may be advantageously replaced by the "Equal Deflection Method." This method was first suggested by Mr. Sherman and worked out by Mr. A. F. Wagner[2] of Purdue University. If a current be used through the primary of the mutual inductance sufficient to produce a deflection d equal to D, equation (3) becomes

$$B = \frac{10^8 Mi_m}{AS} = Ki_m. \tag{4}$$

This wipes out all inaccuracy due to calibration.

[1] Loc. cit.
[2] To be published elsewhere.

PROCEDURE.

In order to investigate the possible influence of the large mass of metal of the testing machine on the bar when clamped in place, so far as compensation was concerned, specimen *A* was tested both in and out of the

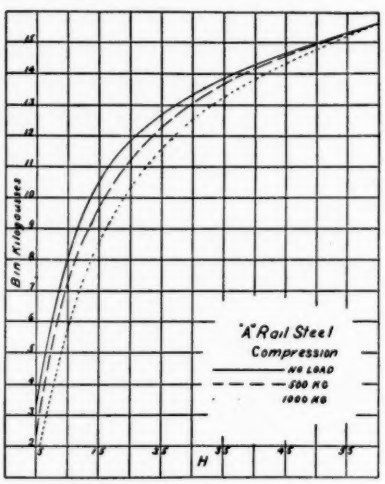

Fig. 4.

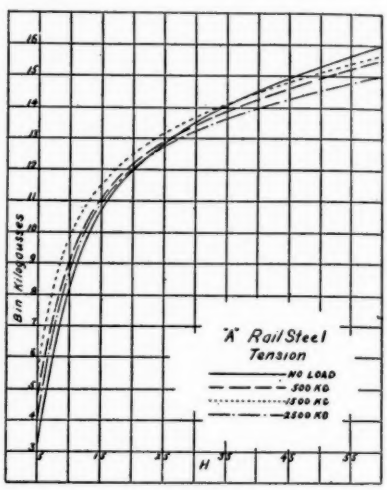

Fig. 5.

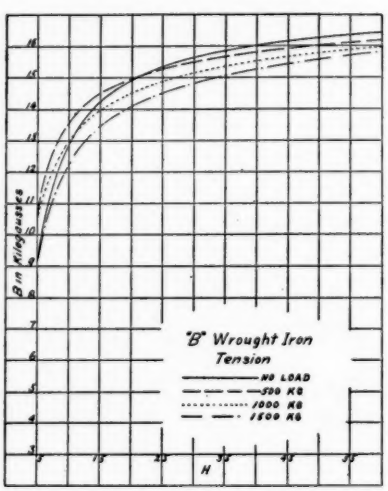

Fig. 6.

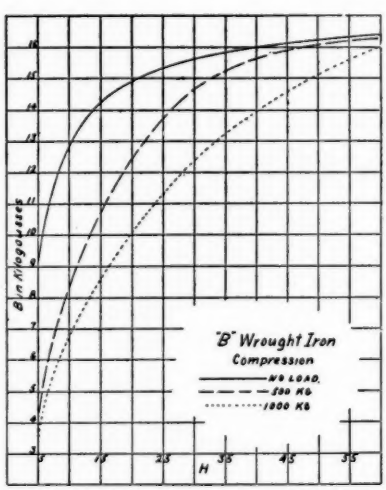

Fig. 7.

machine. The two curves were found to coincide exactly. This investigation is very good evidence of effective compensation, as otherwise the shunting of the test bar with the heavy mass of iron in the testing machine would alter the curve.

Each of the samples tested was about sixty cm. long and one cm. in diameter. The auxiliary bars were of the same cross section and material and were about forty cm. long. At first the samples were put through several cycles of loading to get rid of the effect of previous stress.

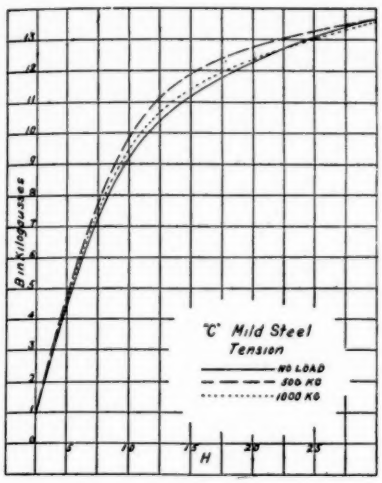

Fig. 8.

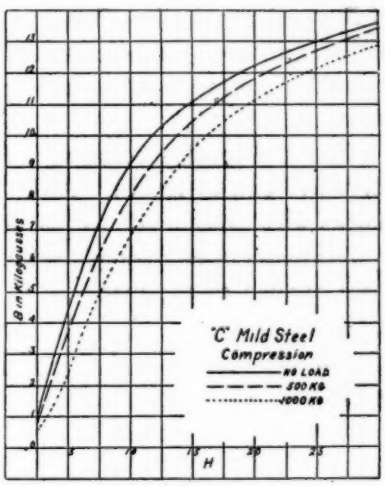

Fig. 9.

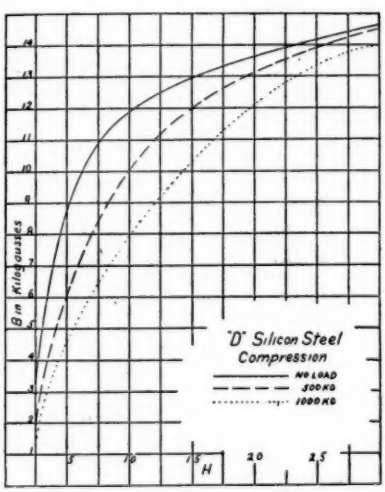

Fig. 10.

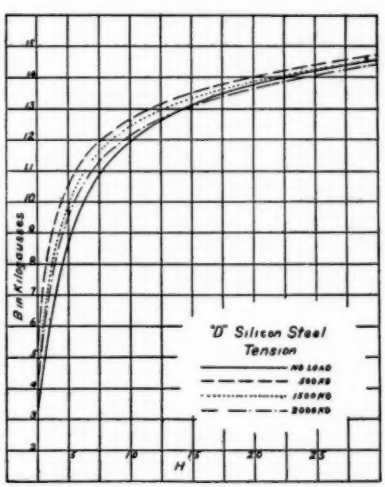

Fig. 11.

After carefully demagnetizing the sample by reversal of direct current, it was subjected to a magnetizing field and by use of the auxiliary and compensating windings, was brought to a uniform state of magnetization. With the sample and permeameter in the machine and no stress applied,

values of B were determined for varying loads and for a fixed value of H, as shown in the previous section. The sample was then put under a stress of 500 kg. per sq. cm. As only the test bar was under stress, the circuit would not be uniform in flux, so the compensating and auxiliary currents had to be changed. When all was again balanced the new value of B was determined. This procedure was continued at steps of 500 kg. per sq. cm. until a load of 2,000 kg. or 2,500 kg. per sq. cm. was reached. The same process was repeated at other values of magnetizing force up to saturation.

After the tension tests were made, the test bars were cut down to forty-five cm. in length. After being placed in the permeameter, iron blocks with holes made to just fit over the bars, were slipped on. The permeameter was then placed in the Olsen machine and compressive force applied to the blocks. The iron blocks served to fix the ends of the rod and thereby allow double the load to be applied without causing measurable side deflection. Compression loads of 500 and 1,000 kg. per sq. cm. were applied and the corresponding B values found as before.

Sample of Data Taken by "Equal Deflection Method."

Bar *A*. Diameter of bar = 0.993 cm.
H constant = 105. *B* constant = 28,120.

I_h = .048	.095	.124	.209
H = 5	10	13	22
R = 5,000	5,000	10,000	10,000
No load.			
D = 3.35	8.73	5.81	7.19
I_m = .112	.290	.350	.434
B = 3,150	8,150	9,840	12,200
1,500 *Kg./Sq. Cm. (Tension).*			
D = 5.10	9.90	6.39	7.53
I_m = .172	.336	.387	.450
B = 4,840	9,460	10,730	12,650
2,000 *Kg./Sq. Cm. (Tension).*			
D = 4.72	9.96	6.30	7.45
I_m = .159	.338	.378	.447
B = 4,470	9,500	10,620	12,560

R = resistance in series with bal. galv.
I_m = calibrating current.

DISCUSSION.

In all the samples tested the Villari reversal effect was found for tension, but not in all cases for compression. From the form of the curves it was thought, however, that reversal would take place at higher values of magnetizing force. All of the samples were magnetically soft and follow the general form of the curves which, according to Ewing,[1] are typical for soft material.

As tension was applied to the specimen at low values of H, the permeability first increased and later, as more tension was applied, the permeability decreased and for heavy tension loads decreased below the original value. Above the Villari critical value this effect was reversed as might be expected. The effect of compression was to decrease the permeability at low values of H and to increase it at high values of H, but in much greater degree than for tension.

It will be seen in comparing the tension and compression curves that, when a bar is placed under compression and a low value of magnetizing force is applied with a successively decreasing load, the permeability gradually increases with a steady decrease in this rate of increase as zero load is approached. If new tension is applied, the permeability still increases at a diminishing rate until a certain value of load is reached at which the increase ceases and reverses, the permeability becoming smaller as more load is applied. The change in rate seems nearly constant, and in the same direction throughout.

PURDUE UNIVERSITY,
June 9, 1914.

[1] Ewing, Magnetic Induction in Iron and Other Metals, 1903 edition.

DIOPTRIC FORMULÆ FOR CYLINDRICAL LENSES COMBINED AT OBLIQUE AXES.

BY CHARLES SHEARD.

THE solution of the problem of transposing double cylinders at oblique angles into their equivalents with axes at right angles (the so-called cross-cylinder combination) was first worked out, as far as the writer is aware, by C. F. Prentice and is given in his book on Ophthalmic Lenses, pages 53–83. His method is somewhat involved and lengthy and the final equations given for obtaining the values of the dioptric powers of the cylinders and their axial angles involve several terms and algebraic processes. The writer of this paper will present in outline a much simpler and clearer solution of the problem. The method of curvatures has doubtless been previously applied to cylinders, but no such solutions as are given in the succeeding paragraphs are known to me. This paper also calls attention to the superiority of the method of curvatures in the solution of a large number of problems in geometrical optics.

In Fig. 1, let *abmcd* represent a cylinder with *op*, its axis, making angles α and β respectively with the Y and X (90° and 0°) axes. The dioptric power in a direction at right angles to the axis *op* and the X, Y plane is determined by the curvature of the cylindrical surface; *i. e.*, by *amb*. Since the dioptric power is the reciprocal of the focal length, and

$$d = \text{dioptric power} = 1/f = (n - 1)1/r,$$

then $d \propto 1/r$. By geometry, $\overline{ap}^2 = 2r \cdot mp - \overline{mp}^2$ and neglecting the term $\overline{mp}^2$,

$$r = \frac{\overline{ap}^2}{2mp},$$

or

$$d \propto \frac{1}{r} \propto \frac{1}{\overline{ap}^2}, \tag{1}$$

since *mp*, the thickness of the cylinder, is a constant for any particular case.[1] Fig. 1 represents a cylinder of definite thickness, *mp*, and definite

[1] The foregoing solution assumes a cylindrical element in which the thickness is very small in comparison to the radius of curvature of the curved surface, which is the case in actual practice. Therefore the arcs obtained by the intersections of the cylinder by planes while actually portions of ellipses may be taken as portions of circles.

semi-chord, ap. If the thickness of the cylinder is kept constant, it will be apparent to the reader that the value of the line ap will be altered when the curvature of the arc amb is changed. Since the width, ab, and the thickness, mp, are constants of a specified cylinder, the chords ab, sb and ak may be used in the measurement of the curvatures of the arcs amb, sfb and afk respectively in the manner indicated in equation (1).

The dioptric power of the cylinder in directions parallel to the X and Y axes may be obtained by passing planes through the cylinder intersecting its cylindrical surface in arcs afk and sfb.

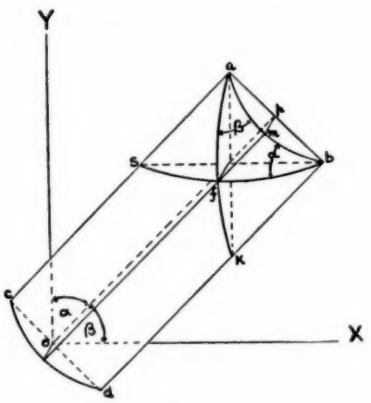

Fig. 1.

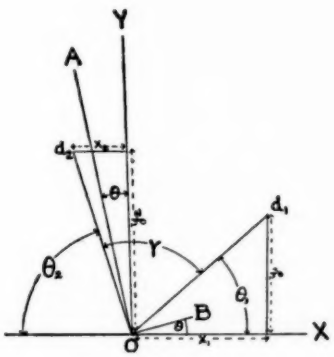

Fig. 2.

Since $ak = ab/\cos\beta$ and $sb = ab/\cos\alpha = ab/\sin\beta$, by substitution in (1) we obtain

(2) d_y = vertical dioptric power = $d\cos^2\alpha = d\sin^2\beta$,
d_x = horizontal dioptric power = $d\cos^2\beta$.

Hence the dioptric powers of any cylinder taken in right-angled directions are proportional respectively to the square of the cosine and sine of the angle which the axis of the cylinder makes with one of the coördinate axes.

In Fig. 2, Od_1 and Od_2 represent graphically the powers, d_1 and d_2, of two cylinders with axes at the oblique angle γ and making angles θ_1 and θ_2 with the X axis. Let OA and OB represent the right-angled equivalents of Od_1 and Od_2. The angle BOA is 90°; θ represents the angle which the axes of the equivalent cylinders make with the X and Y axes. Let the dioptric values of OA and OB be indicated by the symbols A and B.

The total dioptric power of the two cylinders Od_1 and Od_2 is (see Fig. 2)

(a) along X axis, $x_1 + x_2 = d_1\cos^2\theta_1 + d_2\cos^2\theta_2$,

(*b*) along Y axis, $y_1 + y_2 = d_1 \sin^2 \theta_1 + d_2 \sin^2 \theta_2$,

or

$$\Sigma x + \Sigma y = d_1 + d_2 = A + B. \tag{3}$$

$d_1 + d_2$ must be equal to $A + B$ since the sum of the dioptric powers before and after transposition must remain the same.

Treating the cross cylinders A and B, which are to be equivalent to the original oblique-angled combination, in a similar manner it will be seen that

$$A \sin^2 \theta + B \cos^2 \theta = \Sigma x_{A,\,B} = X, \tag{4}$$

$$A \cos^2 \theta + B \sin^2 \theta = \Sigma y_{A,\,B} = Y. \tag{5}$$

Combining by substraction (4) and (5) one obtains

$$(A - B) \sin^2 \theta - (B - A) \cos^2 \theta = \Sigma x_{A,\,B} - \Sigma y_{A,\,B}$$

or

$$(B - A) \cos 2\theta = \Sigma y_{A,\,B} - \Sigma x_{A,\,B} = Y - X \tag{6}$$

and by addition of equations (4) and (5) one obtains

$$A + B = Y + X = d_1 + d_2. \tag{7}$$

Therefore $\Sigma x + \Sigma y$ for cylinders of powers d_1 and d_2 is equal to a similar quantity for cylinders of powers A and B.

If the X, Y axes be rotated until the Y axis coincides in turn with Od_2 and OA it will be seen that

$$\begin{aligned} A^2 + B^2 &= d_1^2 + d_2^2 + 2d_1d_2 \cos^2 \gamma \\ &= (d_1 + d_2)^2 - 2d_1d_2 \sin^2 \gamma, \end{aligned} \tag{8}$$

from which it follows that

$$A \cdot B = d_1d_2 \sin^2 \gamma. \tag{9}$$

Equations (6), (7) and (9) give the complete solution of the problem.

Example.—To transpose 1.50 cyl. ax. 120° + 1.00 cyl. ax. 80° into the equivalent cross cylinder. We have

$$A + B = 2.50, \tag{7}$$

$$A \cdot B = 0.6195, \tag{9}$$

$$(B - A) \cos 2\theta = \Sigma y - \Sigma x = 1.6896. \tag{6}$$

Solving equations (7) and (9), $A = 2.21$ diopters and $B = 0.29$ diopter Equation (6) gives $\theta = 14° 12'$. Hence the solution,

2.21 cyl. ax. 104° 12′ + 0.29 cyl. ax. 14° 12′.

By neutralization there was obtained

2.25 cyl. ax. 104° + 0.25 cyl. ax. 14°

and by Prentice's formulæ

$$2.22 \text{ cyl. ax. } 104^\circ\ 47' + 0.28 \text{ cyl. ax. } 14^\circ\ 47'.$$

Equations (6), (7) and (9) are applicable to the solution of the cross cylinder equivalents of any combination of converging or diverging cylinders if due regard is had for the signs intrinsically associated with the dioptric powers of the cylinders involved. Furthermore, the algebraic sign of the quantity $(Y - X)$ determines the quadrant in which the axis of A or B lies; that is to say, whether A has its axis at an angle θ or $\theta + 90^\circ$.

Tables have been prepared by the writer to facilitate in the calculation of such transpositions.

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RATE OF DECAY OF PHOSPHORESCENCE AT LOW TEMPERATURES.

BY E. H. KENNARD.

THE first attempt to start out from a definite physical assumption and deduce a formula for the rate of decay of phosphorescent light was made in 1891 by H. Becquerel,[1] who obtained the expression

$$I = \frac{I_0}{(1 + \alpha t)^2}, \qquad (1)$$

where I = intensity, t = time. Soon afterward Wiedemann and Schmidt developed their classical theory, according to which phosphorescence is due sometimes to the gradual restoration of a chemical equilibrium that has been disturbed, sometimes to the recombination of ions that have been formed by the exciting cause. If we adopt the latter hypothesis and add certain simple assumptions (cf. equations (2), (3) below) we are led[2] to the same simple expression that was obtained in another way by Becquerel.

This formula appears to hold[3] for the phosphorescence following the electrodeless ring discharge in gases. In solids it holds throughout in some cases,[4] but usually the values that would have to be assigned to I_0 and α undergo a rapid decrease at some point in the process of decay, remaining fairly constant before and after. Many possible causes for this deviation can be imagined: one of the most promising, according to Merritt,[5] is physical heterogeneity. This assumption leads to curves of the observed type, and it is supported by the nature and origin of those substances which show strong and lasting phosphorescence. All are crystalline; in many cases the presence of an impurity seems essential; and they are either crystallized from solution, which is likely to result in segregation of constituents, or are formed by mixing and heating without the occurrence of melting.

To test the explanation further, it seems desirable to obtain curves

[1] Cf. Kayser, Handbuch der Spectroscopie, IV., p. 717.
[2] Nichols and Merritt, PHYS. REV., 22, p. 279, 1906.
[3] Trowbridge, PHYS. REV. 26, p. 515, 1908.
[4] Cf. C. A. Pierce, PHYS. REV. 26, p. 312 and p. 454, 1908.
[5] PHYS. REV., 27, p. 367, 1908.

for a number of amorphous solids which at some temperature have been liquid and therefore homogeneous. This condition is satisfied by many substances that phosphoresce at low temperatures, and accordingly the temperature of liquid air was chosen in the present investigation.

APPARATUS.

The specimen, *S* (Fig. 1), was supported on the end of a brass tube, *B*, dipping into liquid air (*A*); the tube was screwed into a brass cup, *C*, which helped to keep the temperature of the specimen uniform. Over this was a tin hood (*H*) carrying two windows, one of quartz (*W*) to admit the ultra-violet exciting light from a mercury vapor lamp (*M*) and the other of glass to allow the phosphorescent light from the specimen to fall on a potassium amalgam photo-electric cell (furnished by Muller-Uri). Just above the windows were mounted three shutters (*T*) by which the exciting light could be cut off and the cell exposed to the phosphorescent light and then again screened. The platinum terminal of the cell was connected to an electrometer while the amalgam was subjected to a negative potential of a few volts.

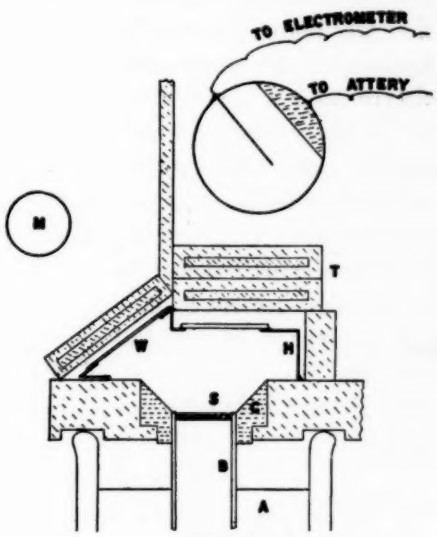

Fig. 1.

The shutters consisted of wooden slides drawn by phosphor-bronze springs; they were released by electromagnets which were operated by mercury keys tripped by a seconds pendulum swinging in an arc of about 24°. Often however, the second shutter was released by the first and followed it about 0.02 second behind, so that exposure began almost immediately after the exciting light was cut off.

The intervals of time at which the shutters followed each other, if longer than a second, were calculated from the position of the keys and the period of the pendulum. Otherwise all intervals were measured in subsidiary experiments by means of a ballistic galvanometer: one shutter was made to open a shunt and thus to cause a certain current to flow through the galvanometer, the next, to open another shunt and thereby to stop the current. The calculation of the interval involves

only the period of the galvanometer and the ratios of resistances. The accuracy of these measurements is discussed below.

The slowest shutter required about 1/150 sec. to close the opening (about 23 mm. square) not counting the rather longer flying start and the time lag of the electromagnet.

The formation of frost inside the hood was slight and caused no trouble, but in order to stop the deposition of frost on the outside of the windows it was found necessary to blow a steady stream of dry air over the hood.

OPERATION.

In taking a run, the mercury lamp was first started and given at least half an hour to warm up. Meanwhile, the liquid air was applied and time was allowed for the specimen to become thoroughly cooled. Fresh liquid air was usually added every 20 min. For each observation, the electrometer was insulated and the zero point determined; after 30 sec. an auxiliary shutter was opened and excitation began; 30 sec. later another scale reading was taken and the pendulum was released, thus operating the shutters at the desired intervals; after 60 sec. (usually) another scale reading was taken and after another minute a fourth; the electrometer was then earthed. The extra readings allowed correction for the ever-present leak.

For instance, in a typical case the second shutter exposed the cell 0.02 sec. after the first had cut off the exciting light and 9.93 sec. later the third shutter ended the exposure; the four readings at intervals of 1 min. were:

303.2 302.3 372.4 371.3

The electrometer having been this time at its final potential during practically the whole of the minute between the second and the third readings, the correction for the leak is $372.4 - 371.3 = 1.1$, and the corrected deflection is $372.4 - 302.3 + 1.1 = 71.2$ mm.

Usually seven to ten points on the curve were determined and the series was then at once repeated in reverse order. Where possible the total emission from the start was measured in each observation, but in the case of paraffine it was necessary to measure separately successive portions of the emission and then add the deflections together.

SUBSIDIARY OBSERVATIONS.

A little uncertainty attaches to the intervals of time involved, but the error in the results due to this source is relatively small. The calculated times must be accurate within 1/50 sec., since the velocity of the pendulum past each key and the velocity of separation of wire and mercury

were not less than 35 cm. per sec. Measurements of the 0.6 interval gave 0.602, 0.600, 0.598 sec. on three separate days, the ballistic galvanometer readings on each day agreeing within 1 per cent.; similarly 0.310, 0.309 sec. with the same agreement for another interval. When the first shutter was releasing the second the interval between them came out 0.022, 0.021 sec. with several per cent. variation. The degree of agreement of these observations is a test both of their own accuracy and of the uniformity with which the shutters operated. It may accordingly be asserted with confidence that each time interval occurring in the main experiment was known both within 10 per cent. (when small) and within 1/50 sec.

It has been shown by Richtmyer, Elster and Geitel, and others that a steady photo-electric current under a small potential difference is proportional to the intensity of the light. But there might still be a time lag in the action of the cell sufficient to introduce an error into measurements of short-time emission. So a tiny carbon lamp fed by a constant current from storage cells was substituted for the specimen and a double run with varying times of exposure was taken. The results, given below, show no sign of appreciable lag in the photo-electric cell down to exposures of 0.1 sec. t is the interval of exposure (corrected

	δ			
t	*Down*	*Up*	*Mean*	δ/t
0.097 sec.	28.4	28.0	28.2	291
0.193	55.2	54.9	55.1	285
0.297	87.6	86.7	87.2	293
0.394	114.8	114.1	114.5	291
0.493	143.2	144.3	143.8	291
0.587	172.7		172.7	294

for measured differences between the shutters by subtracting 0.011 sec.), δ is the deflection of the electrometer in mm. corrected for leak.

PRINCIPAL OBSERVATIONS.

The results obtained thus far on paraffine are shown in the tables and in Fig. 2; some observations on cetyl alcohol and kerosene are exhibited in Fig. 3. In the tables, E_1 and E_2 denote the total emission of phosphorescent light from 0.02 sec. up to time t, where t is measured from the instant at which the exciting light was cut off; the observations for E_1 were taken in the order of increasing intervals, while those for E_2 followed immediately in reverse order. E is the mean of E_1 and E_2. As only relative values are desired, the emission of light is expressed in mm.

of deflection of the electrometer produced by the photo-electric emission caused by the light.

In order to test the theoretical formulas, the value of $R = (t - 0.02) \div E$ is given in the tables for each observation, and it is this quantity

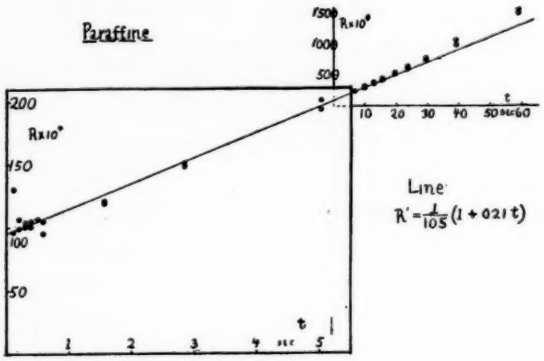

Fig. 2.

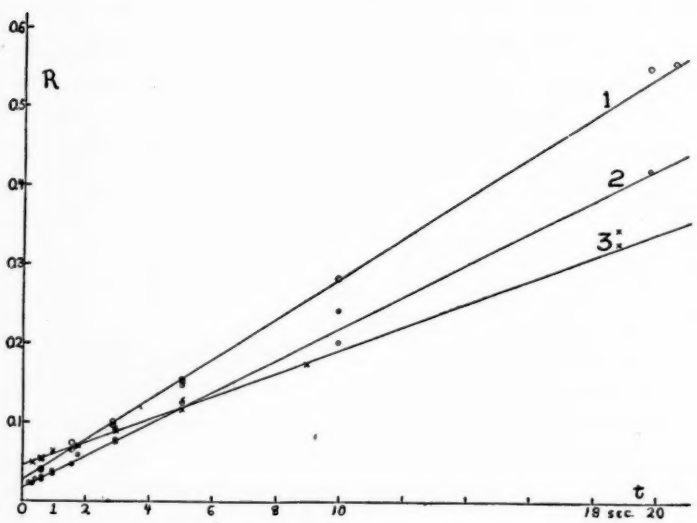

Fig. 3.

(1) Cetyl alcohol: $R' = \frac{1}{36.3}(1 + 0.92t)$. (2) Cetyl alcohol: $R' = \frac{1}{57.8}(1 + 1.16t)$.

(3) Kerosene: $R' = \frac{1}{22}(1 + 0.32t)$.

that is shown on the plots. Fig. 1 contains values of R corresponding to E_1 and E_2 in Table I.

Table I.

Paraffine.

t	E_1	E_2	E	$R\times10^4$	$R'\times10^4$	$R''\times10^4$	δ
0.02							
0.60	65.8	64.5	65.15	89	92	92	+ 5
1.56	139.8	135.4	137.6	112	111	112	0
2.85	207.4	202.7	205.05	138	136	136	− 2
5.03	278.8	277.9	278.35	180	179	178	− 2
9.95	361.5	358.3	359.9	276	275	276	0
19.6	409.8	403.6	406.7	482	465	486	+ 4
59.1	424.7	419.2	421.95	1,400	1,237	1,418	+18

$$R' = \frac{1 + 0.243t}{124}, \quad \delta = R'' - R$$

$$R'' = \frac{1}{119.7}\frac{.14(t - 0.02)}{1 - e^{-.14(t-00.2)}} + .147(t - 0.02).$$

Table II.

Paraffine.

t sec.	E_1 div.	E_2 div.	E div.	$R\times10^4$	$R'\times10^4$	$R''\times10^4$	δ
0.022							
0.105	8.9	6.4	7.65	108	97	98	−10
0.201	18.3	16.7	17.5	102	99	100	− 2
0.306	28.2	27.4	27.8	102	101	102	0
0.402	37.6	36.3	36.9	103	103	104	+ 1
0.501	44.8	44.8	44.8	107	105	106	− 1
0.595	55.2	60.5	57.8	99	107	108	+ 9
1.56	130.5	126.4	128.4	120	126	126	+ 6
2.85	191.6	186.7	189.1	150	152	151	+ 1
5.03	260.2	250.4	255.3	196	196	195	− 1
6.80	296.8	283.9	290.3	234	231	231	− 3
9.95	345.5	321.6	333.5	298	294	298	0
12.9	367.6	342.3	354.9	363	353	364	+ 1
15.7	378.3	355.7	367.0	427	409	428	+ 1
19.6	388.7	366.3	377.5	519	487	520	+ 1
23.6	397.8	372.2	385.0	612	567	616	+ 4
29.5	402.7	371.1	386.9	762	686	761	− 1
39.3	400.1	372.8	386.4	1,015	882	1,006	− 9
59.1	396.7	377.5	387.1	1,527	1,276	1,514	−13

$$R' = \frac{1}{105}(1 + 0.21t), \quad \delta = R'' - R$$

$$R'' = \frac{1}{103.5}\left\{\frac{0.14(t - 0.02)}{1 - e^{-0.14(t-0.02)}} + 0.125(t - 0.02)\right\}.$$

If formula (1) mentioned above holds, the curve for R should be a straight line. For we have

$$I = \frac{I_0}{(1 + at)^2}, \tag{1}$$

$$E = \int_{t_1}^{t} I dt = \frac{I_0(t - t_1)}{(1 + at_1)(1 + at)},$$

$$R = \frac{t - t_1}{E} = \frac{1 + at_1}{I_0}(1 + at), \tag{2}$$

and R is linear in t. In the present case $t_1 = 0.02$ sec. Arbitrary values were assigned to the constants in (2) and theoretical values of R were then computed. These are shown under the heading R' in the tables and are represented by the straight lines drawn on the plots. The numerical formula for R' is given in each case.

Each table and each curve in Fig. 3 represents a double series obtained on a separate day. The different series are in general not comparable as to magnitude of emission, and probably not entirely as to shape because the intensity of excitation varies.

But even the two parts of each double series do not agree very well. In the case of paraffine, the variation looks at first sight like weak "hysteresis." But in the other cases, the variations are erratic. As a further test five observations on kerosene, the interval being from 0.02 to 2.95 sec. after excitation, gave 31.3, 33.0, 33.3, 34.6, 30.8, the outgoing and returning readings in the double series just preceding (Curve 3) being 31.5, 34.3 respectively. The most probable cause of all these variations would seem to lie in fluctuations of the exciting light, which would result in variations of initial intensity.

The results seem however sufficient to warrant the conclusion that in the three substances examined R is linear in t and formula (1) holds at least during the first 10 seconds of decay, or until the phosphorescence has sunk to 1/10 or less of its initial value. Paraffine then shows a decided upward bend in the curve, which means that the decay is occurring more rapidly than is required by the formula. This cannot be due to the presence of several emission bands in the spectrum, each obeying (1), for it may easily be shown that such a combination would produce a downward bend in the curve. Paraffine thus differs radically from the ordinary phosphorescent substances, which exhibit an initial rapid decay. If any such effect exists here, it must at least be very weak or of extremely short duration.

It is interesting to consider what modification of the ionization theory

would lead to a curve of the observed type. Nichols and Merritt[1] obtained from their assumptions the equations

$$\frac{dn}{dt} = -kn^2, \tag{3}$$

$$I = -A\frac{dn}{dt}, \tag{4}$$

where n = number of phosphorescent nuclei or of corresponding ejected electrons (or other ions) present, I = intensity of phosphorescence during decay. Hence

$$n = \frac{n_0}{1 + kn_0t}, \tag{1}$$

$$I = \frac{I_0}{(1 + at)^2}$$

where $a = kn_0$, $I_0 = Akn_0^2$.

The unusually rapid later decay suggests that something else besides the ejected electrons is destroying the phosphorescent nuclei. If we suppose that the ordinary free electrons may unite with a positive phosphorescent nucleus and cause luminescence (but that no luminescence arises from their normal recombination with an ordinary positive atom which has lost a free electron), we are led to the modified equation

$$\frac{dn}{dt} = -kn^2 - k'mn, \tag{5}$$

where m = number of free electrons. If m is practically uninfluenced by the presence of the electrons ejected from phosphorescent nuclei and is therefore practically constant, and if as before

$$I = -A\frac{dn}{dt},$$

we obtain after integrating

$$I = \frac{I_0e^{-\beta t}}{\left[1 + \frac{\alpha}{\beta}(1 - e^{-\beta t})\right]^2}, \tag{6}$$

where $\alpha = kn_0$, $\beta = k'm$, $I_0 = A(\alpha + \beta)n_0$, n_0 being the initial number of phosphorescent nuclei present.

It is evident from the deduction of (6), or by substituting in it $t = t_1 + (t - t_1)$, that the form of the right-hand member is unaltered if $t - t_1$ be taken as the variable instead of t, provided that I_0 be replaced by I_2, and α by α_1 to correspond to the displaced starting-point.

[1] Nichols and Merritt, PHYS. REV., 22, p. 279, 1906.

Hence by integration

$$E(t_1, t) = \frac{I_1}{\beta} \frac{1 - e^{-\beta(t-t_1)}}{1 + \frac{\alpha_1}{\beta}(1 - e^{-\beta(t-t_1)})}, \tag{7}$$

and if $R = (t - t_1)/[E(t_1, t)]$

$$R = \frac{1}{I_1}\left[\frac{\beta t}{1 - e^{-\beta(t-t_1)}} + \alpha_1 t\right]. \tag{8}$$

Under the heading R'' in the tables are given values of R calculated from (8) in the numerical form given below the tables: the same value of β was designedly employed in both cases because theoretically it seems unlikely that it should vary from day to day. They agree rather well with the observed values given under R, which indicates that (6) represents the decay of the phosphorescence fairly well. But the accuracy of the observations is not sufficient definitely to establish any three-constant formula.

SUMMARY.

1. The rate of decay of phosphorescence at liquid air temperatures was studied in paraffine, cetyl alcohol and kerosene, employing a photoelectric cell and an electrometer.

2. From 0.1 sec. to 10 sec. paraffine obeys the law

$$I = \frac{I_0}{(1 + at)^2};$$

then the decay is more rapid (whereas in crystalline substances at ordinary temperatures the later decay is less rapid). Cetyl alcohol and kerosene appeared to obey this law as far as their phosphorescence could be followed (20 sec.).

3. Taking into account the free electrons, assumed constant in number, the formula becomes

$$I = \frac{I_0 e^{-\beta t}}{\left[1 + \frac{\alpha}{\beta}(1 - e^{-\beta t})\right]^2},$$

which represents the decay for paraffine within the fairly large errors of observation.

It is a pleasure to acknowledge my obligations to Professor E. Merritt for suggesting the problem and for advice in regard to the low temperature arrangements, and to Professor G. S. Moler for advice regarding the shutters.

CORNELL UNIVERSITY,
May, 1914.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

THE SPECIFIC HEATS OF MIXTURES OF ALCOHOL AND WATER AND OF SOLUTIONS OF NON-ELECTROLYTES IN THESE MIXTURES.[1]

BY WILLIAM FRANCIS MAGIE.

THE specific heats were determined of mixtures of one gram-molecule of ethyl alcohol with N gram-molecules of water. Between the limits $N = 5$ and $N = 50$ the heat capacity of such a mixture is very exactly obtained by adding to the heat capacity of the water, $18N$, the value ζ of the apparent heat capacity of the alcohol, given by the formula

$$\zeta = aN + \frac{b}{N} + c,$$

$$a = -0.0666, \quad b = -95.8, \quad c = 67.00.$$

For $N = 100$ or more, and for $N = 3$, this formula does not hold.

A gram-molecule of pyrocatechin dissolved in considerable water has an apparent heat capacity of 75.5, and in alcohol an apparent heat capacity of 57, independent of the concentration. When dissolved in mixtures of the sort described above the apparent heat capacity is apparently independent of the concentration of the pyrocatechin in a particular mixture, but differs with the proportion of alcohol in the mixture. The following table gives the results of the measurements. From 10 to 15 grms. of pyrocatechin were dissolved in about 700 grms. of the mixture. The N of the table represents the number of gram-molecules of water mixed with one gram-molecule of alcohol. The ζ represents the apparent heat capacity of the pyrocatechin.

N	50	25	12.5	8	5	3
ζ	70	61	49	35	34	53.5

The lowest values found are equal to the heat capacity of a gram-molecule of solid pyrocatechin.

Similar results were obtained for resorcin, except that the minimum value of ζ is considerably below that found for solid resorcin.

The only conceivable explanation of these results is that some association occurs in the solution, whereby the degrees of freedom of its constituents are diminished in number.

[1] Abstract of a paper presented at the Washington meeting of the American Physical Society, April 24, 1914.

THE VILLARI CRITICAL POINT IN FERROMAGNETIC SUBSTANCES.[1]

BY S. R. WILLIAMS.

UNDER this subject a comparative study has been made of the change in length effect due to magnetization with the change in magnetization arising from a longitudinal pull. The first phenomenon is known as the Joule magnetostrictive effect and the second as the Villari reversal effect. The results indicate that for those substances in which a reversal of the Joule effect occurs, there also appears a Villari reversal. Specimens showing only an elongation for all field strengths exhibit only an increase of magnetization due to a longitudinal pull, while those rods, in which contraction for all field strengths appears, manifest a decrease of magnetization due to a longitudinal pull.

Nickel is the most interesting of all the specimens studied. It can be made to exhibit or not exhibit a Joule reversal and also a Villari reversal effect depending upon whether or not complete demagnetization has been previously secured. This is an important point and will doubtless clear up the controversy between the various investigators of this subject.

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[1] Abstract of a paper read by title at the New York meeting of the Physical Society, February 28, 1914.